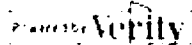




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UEDA YUMIKO**Assignee:** NIPPON SHOKUBAI CO LTD[News, Profiles, Stocks and More about this company](#)**Published / Filed:** 1999-06-29 / 1997-12-12**Application Number:** JP1997000343377**IPC Code:** Advanced: C09D 5/00; C09D 7/12.
Core: more
IPC-7: C09D 5/00; C09D 7/12.**Priority Number:** 1997-12-12 JP1997000343377**Abstract:** **PROBLEM TO BE SOLVED:** To obtain a destaticizing coating material composition capable of forming coated film having low dependence on humidity, temperature or the like, having stable destaticizing properties for a long period of time, excellent in optical physical properties such as transparency, colorlessness, durability, adhesivity and flexibility, or the like, and its use.**SOLUTION:** In this destaticizing coating material composition comprising a binder component having film-forming performances, a trivalent and/or a tetravalent metal element (M₁) and Zn as metal components and zinc oxide-based particles showing zinc oxide crystallinity in terms of X-ray diffraction, the zinc oxide-based particles have the ratio of the total content of impurities H composed of a halogen metal ion and/or atom except F, sulfate SO₄²⁻ and nitrate NO₃⁻ to the number of zinc atoms (with the proviso that the number is calculated as the number of S atoms in the case of sulfate group and as the number of N atoms in the case of nitrate group) of ≤0.5%.

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Family: None**Other Abstract Info:** DERABS C1999-425181 DERABS C1999-425181[Don't waste this for the Gallery](#)

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Derwent Title: Antistatic paint composition for glass, ceramics and resin substrates - comprises binder component having film formability and zinc oxide-based particles containing trivalent and/or tetravalent metal element and specified impurities

Original Title: ☒ JP11172153A2 DESTATICIZING COATING MATERIAL COMPOSITION AND ITS USE

Assignee: NIPPON SHOKUBAI CO LTD Standard company
Other publications from NIPPON SHOKUBAI CO LTD (JAPCO)

Inventor: TAKEDA M; UEDA Y;

Accession/ 1999-425181 / 199939

Update:

IPC Code: C09D 5/00 ; C09D 7/12 ;

Derwent Classes: G02 L01; L02;

Manual Codes: G02-A05B(Other coating compositions for electrical or magnetic material (exc. wire)) , L01-F03A(Surface treatment of glass fibre) , L01-G04B(Coating glass sheet with organic material) , L01-G09(Decorating glass) , L02-A07 (Refractones, ceramics, cement manufacture - decorating and glazing)

Derwent Abstract: { JP11172153A) An antistatic paint composition comprises a binder component having film formability and zinc oxide-based particles containing a trivalent and/or tetravalent metal element (M) and Zn as the metal component and showing zinc oxide crystallinity in X-ray diffraction methodology. The zinc oxide-based particles have an atomic ratio of the total H as impurity comprising ion and/or atom of halogen except F, sulphonic acid radical and nitric acid radical to Zn of up to 0.5 by atomic number (using atomic number of S in sulphonic acid radical and atomic number of N in nitric acid radical). Also claimed is a coated article having a film made of the antistatic paint composition on the surface of the substrate thereof.
Use - The antistatic paint composition is applied to a substrate of glass, ceramics, resin and more preferably to a film or fiber thereof.
Advantage - The antistatic paint composition forms a film improved in optical property, durability, adhesion and flexibility less depending on humidity nor temperature. The coated article by the composition retains stable antistatic property for a long time.

Dwg 0-0

Family: PDF Patent Pub. Date Derwent Update Pages Language IPC Code

☒ JP11172153A * 1999-06-29 199936 22 English C09D 5:00

Local app's: JP1997000343377 Filed 1997-12-12 (97JP-0343377)

Priority Number:

Application Number	Filed	Original Title
JP1997000343377	1997-12-12	DESTATICIZING COATING MATERIAL COMPOSITION AND ITS USE

Extended Polymer Index: Show extended polymer index

Title Terms: ANTISTATIC PAINT COMPOSITION GLASS CERAMIC RESIN SUBSTRATE COMPRISE BIND COMPONENT FILM FORMING ZINC OXIDE BASED PARTICLE CONTAIN TRIVALENT METAL ELEMENT SPECIFIED IMPURE

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CLAIMS

[Claim(s)]

[Claim 1]In an antistatic coating constituent containing zinc oxide system particles which use as a metallic component a binder component which has film formation performance, and a metallic element (Md) and Zn which take trivalent and/or tetravalence, and show zinc oxide crystal nature in X diffraction study, Ion and/or an atom of a halogen excluding [said zinc oxide system particle] F, an atomic number [as opposed to zinc in a total content of the impurity H which consists of sulfuric acid root SO_4^{2-} and nitric acid root NO_3^-] (however, in the case of a sulfuric acid root, in the case of an atomic number of S, and a nitric acid root, it calculates as an atomic number of N) -- an antistatic coating constituent characterized by what is been 0.5% or less in a ratio.

[Claim 2]When a diffraction peak with said zinc oxide system particle peculiar to a crystalline zinc oxide appears and it asks for the size $D_s(hkl)$ of vertical microcrystal from two lattice planes (100) and (002) using the Scherrer method (Cauchy approximation of function), When setting to D_w a size of microcrystal which satisfied $D_s(002)/D_s(100) < 2$ and for which it asked using Wilson's method, it is $1 \leq D_w \leq 100$ (nm).

The antistatic coating constituent according to claim 1 which are the zinc oxide system particles to satisfy.

[Claim 3]The antistatic coating constituent according to claim 1 or 2 which is a metallic element excluding [Md] IIIB fellows and IVB fellows.

[Claim 4]An antistatic coating constituent given in either from Claim 1 to 3 whose rate over solid content of said binder component of said zinc oxide system particle and the zinc oxide system particle total quantity is 50 to 95 weight %.

[Claim 5]An antistatic coating constituent given in either from Claim 1 to 3 which contains a conductive adjuvant further.

[Claim 6]A paint article which forms a coat obtained from an antistatic coating constituent of a description by either from Claim 1 to 5 on the surface of a base material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an antistatic coating constituent and its use.

[0002]

[Description of the Prior Art]Conventionally, as an antistatic coating constituent, the paint which contains the surface-active agent of metal particle; anionic systems, such as conductive-metallic-oxide particle; copper, such as a zinc oxide system and a tin oxide system, and nickel, a cation system, and both sexes, etc. as a spray for preventing static electricity is known. Among these, with the constituent containing particles, such as a metallic oxide and metal, the particle diameter of particles was large, or since the dispersibility in the inside of a paint and a coat was insufficient, it excelled in transparency, and the antistatic film without coloring was not obtained. In order to give antistatic property, it is necessary to include many particles in a paint, and it cannot be satisfied, even if neither the flexibility of a coat, nor adhesion, weatherability which are obtained are enough and use a coat as an antistatic film.

[0003]Environment dependency, such as the antistatic property under low humidity being insufficient, and being on the other hand, based on a transmission machine style peculiar to a surface-active agent, although the coat which is excellent in transparency is obtained in the paint which contains a surface-active agent as a spray for preventing static electricity, was high. Since the weatherability of the surface-active agent which is a spray for preventing static electricity was low, the endurance of the coat was not enough, when long term use was carried out, the coat deteriorated and there were various problems with practical coloring arising, or a surface-active agent carrying out bleeding, and antistatic performances falling, or blocking arising etc.

[0004]

[Problem to be solved by the invention]The issue which this invention tends to solve is providing the antistatic coating constituent which can form the coat which the dependency over humidity, temperature, etc. is low, has the antistatic property stable for a long period of time, and is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility, and its use.

[0005]

[Means for solving problem]The binder component in which the antistatic coating constituent concerning this invention has film formation performance, In the antistatic coating constituent containing the zinc oxide system particles which use as a metallic component the metallic element (Md) and Zn which take trivalent and/or tetravalence, and show zinc oxide crystal nature in X diffraction study, The ion and/or atom of a halogen excluding [said zinc oxide system particle] F, an atomic number [as opposed to zinc in the total content of the impurity H which consists of sulfuric acid root SO_4^{2-} and nitric acid root NO_3^-] (however, in the case of a sulfuric acid root, in the case of the atomic number of S, and a nitric acid root, it calculates as an atomic number of N) -- the antistatic coating constituent characterized by what is been 0.5% or less in a ratio.

[0006]When a diffraction peak with said zinc oxide system particle peculiar to a crystalline zinc oxide appears and it asks for the size D_s (hkl) of vertical microcrystal from two lattice planes (100) and (002) using the Scherrer method (Cauchy approximation of function), When setting to D_w the size of microcrystal which satisfied $D_s(002)/D_s(100) < 2$ and for which it asked using the Wilson's method, it is $1 \leq D_w \leq 100$ (nm).

It is preferred that they are the zinc oxide system particles to satisfy.

[0007]As for this antistatic coating constituent, it is preferred that a conductive adjuvant is included further. The paint article concerning this invention is a paint article which forms the coat obtained from the above-mentioned antistatic coating constituent on the surface of a base material.

[0008]

[Mode for carrying out the invention]Below, first, after explaining zinc oxide system particles, a binder component is explained and, finally the antistatic coating constituent and paint article of this invention are explained.

[Zinc oxide system particles] Their dependency over humidity, temperature, etc. is low, and the zinc oxide system particles used by this invention show the antistatic property stable for a long period of time while they show infrared impermeability, conductivity, etc. in addition to the original ultraviolet-rays cover nature of zinc oxide system particles, and a visible light transmittance state.

[0009]Zinc oxide system particles use as a metallic component the metallic element (Md) and Zn which take trivalent and/or tetravalence. The content of Md is expressed with the ratio of the atomic number of Md to the total atomic number of this metallic component, and it is preferred that it is 0.1 to 20%, and it is 3 to 8% still more preferably 1 to 10% more preferably. If less [if it exceeds said range, it will be hard to become the particles which are rich in homogeneity, such as a presentation and a crystal size, and] than said range, infrared cover nature including a heat ray will become insufficient, and antistatic property will fall.

[0010]As Md which is an alloying element, B, aluminum, Ga, In, Tl, C, Si, Ti, Zr, Sc and Y, Hf besides IIIB group elements, such as germanium, Sn, and Pb, and an IVB group element, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Rv, Os, Rh, Ir, La, Ce, Sb, etc. are mentioned. The zinc oxide system particles used by this invention need to show zinc oxide crystal nature in X diffraction study.

[0011]It is the point of excelling in the permeability over the light of a visible light wavelength region, and infrared interception nature as particle diameter of the primary particle of zinc oxide system particles, It is preferred that the crystallite diameter D_w for which it asked using the Wilson's method (the Wilson method) is 1-50 nm (0.001-0.05 micrometer), and it is preferred to distribute without these primary particles condensing the 2nd order. As for the distributed particle diameter D_d of zinc oxide system particles, it is preferred that it is 1 micrometer or less from the point, i.e., the point which improve transparency and gives optical properties, such as colorlessness, of not affecting substantially the hue of the constituent obtained when a transparent feeling is high and adds to a constituent. 0.5 micrometer or less is 0.1 micrometer or less still more preferably more preferably. Especially 0.05 micrometer or less is preferred. It is preferred that points, such as transparency, adhesion, and weatherability, to monodisperse nature is high. monodisperse nature -- a ratio with the crystallite diameters D_w and D_d -- it defines as $R (D_d/D_w)$, it is preferred that R is ten or less, it is more preferred that it is three or less, and 1.5 especially or less are preferred.

[0012]Distributed particle diameter is the mean particle diameter of the weight

reference which can be measured by dynamic light scattering, a centrifuge, etc. In the case of 0.1 micrometers or more, the former measuring method is measured by the latter measuring method at the case below 0.1 micrometer. As zinc oxide system particles used by this invention, polymer constitutes a matrix, the thing (polymer composite particles) of the form which particles are distributing in this matrix is also contained, and it excels that it is hollow shape in optical diffusional permeability. Although the content in particular of the zinc oxide system particles in this particle is not limited, it is desirable that it is 50 to 95 weight % of a range to the complex particle whole quantity in zinc oxide conversion.

[0013] As polymer used for composite-ization, acrylic resin system polymer, alkyd resin system polymer, Amino resin system polymer, polyvinyl resin system polymer, epoxy resin system polymer, Polyamide resin system polymer, polyimide resin system polymer, polyurethane resin system polymer, Polyester resin system polymer, phenol resin system polymer, organopolysiloxane system polymer, The others which are acrylic-silicone-resin system polymer, a polyalkylene glycol, etc., Polyolefin system polymer, such as polyethylene and polypropylene, polystyrene system polymer, Thermoplasticity or thermosetting resin, such as a fluoro-resin system; synthetic rubbers, such as ethylene-propylene copolymerization rubber, polybutadiene rubber, and an acrylonitrile butadiene rubber, crude rubber; polysiloxane group content polymer, etc. can be mentioned.

[0014] As form of a complex particle, as for the surface of a complex particle, although there is no limitation in particular, it is preferred that it is rich in unevenness nature. When unevenness is shown in the surface, it is because compatibility with a binder component etc. becomes high in the coat containing a complex particle. Especially as mean particle diameter of a complex particle, although not limited, it is usually the range of 0.001-10 micrometers. Zinc oxide system particles have a preferred thing which are the purposes, such as weatherability grant by photocatalyst activity reduction with compatibility with the binder component which has the below-mentioned film formation ability, the dispersibility in the inside of an antistatic coating constituent, a dispersion stability, and a zinc oxide, and it comes to process by a surface modification agent.

[0015] Although the above mentioned polymer can also be used as a desirable surface modification agent, the compound containing a M-X group is mentioned from the purpose of weatherability grant. However, X is at least one sort chosen from a hydrogen atom, a halogen atom, and OR^1 , R^1 is at least one sort chosen from the group which consists of a hydrogen atom, the alkyl group which may be replaced, a cycloalkyl group, an aryl group, an aralkyl group, and an acyl group, and at least one sort of M chosen from a metallic element and the group which consists of Si, Ti, Zr, and aluminum especially is preferred. From a viewpoint of grant of dispersibility (dispersibility to a paint or a solvent, stability of a paint, etc.), the polymer which has an organic high polymer chain is mentioned. It is polymer which a thing desirable by both sides of weatherability and dispersibility contains a M-X group, and has an organic high polymer chain, for example, polysiloxane group content polymer, acrylic silicone, etc. are mentioned.

[0016] As for zinc oxide system particles, it is preferred that are an atomic ratio of Ma to Md and the univalent or divalent metallic element Ma is included in $0.00001 \leq Ma/Md < 1$. It is more preferred that it is the range of $0.0001 \leq Ma/Md \leq 0.4$. It is preferred that it is 0.0001 to 2% of range at an atomic ratio to zinc. An existence effect of Ma makes Md contain homogeneously during a ZnO crystal (in monomeric state), moreover stabilizes a crystal surface, and is at a point which controls secondary

condensation and crystal growth. Therefore, it becomes a detailed high crystal of monodisperse nature. Therefore, it also becomes possible to raise antistatic property and infrared cover nature, increasing the amount of Md and excelling in transparency. Although it is indicated by JP,H8-253317,A that existence of an alkaline metal and alkaline-earth metals is not preferred (the 5th page 7th column lines 40-47), the above effects are done so by containing positively in a mentioned range. If there are too few amounts of Ma(s), an effect will not be revealed, and if there are too many amounts of Ma(s), the weatherability of a coat containing these particles may fall. In the univalent or divalent metallic element Ma, it is an alkali metal and/or an alkali earth metal element, and lithium, sodium, potassium, a rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, etc. are mentioned.

[0017]A halogen (.) excluding [zinc oxide system particles used by this invention] F Namely, ion and/or an atom of the chlorine Cl, the bromine Br, and iodine I, an atomic number [as opposed to zinc in a total content of sulfuric acid root SO_4^{2-} and nitric acid root NO_3^- (the impurity H)] (however, in the case of a sulfuric acid root, in the case of an atomic number of S, and a nitric acid root, it calculates as an atomic number of N) -- it is important that it is 0.5% or less in a ratio. It is 0.001% or less especially preferably 0.01% or less still more preferably 0.1% or less more preferably. Also when the impurity H is not included at all, it contains in this. Only when the impurity H is not contained, or it contains and it does not exceed this range, it becomes the particles excellent in monodisperse nature, and a coat excellent in adhesion or weatherability can be formed as well as transparency.

[0018]Zinc oxide system particles used by this invention are preferred in it being a thing which is a diffraction peak peculiar to a crystalline zinc oxide and which shows a diffraction peak to a lattice plane (100), (002), and (101), and fills the following microcrystal parameters. When it asks for the size D_s (hkl) of vertical microcrystal from each diffracting plane (hkl) using the Scherrer method (the Scherrer method) (Cauchy approximation of function), i.e., the Cauchy approximation of function, $D_s(002)/D_s(100) < 2$ is satisfied. It is $0.5 < D_s(002)/D_s(100) < 1.0$ preferably [it is more desirable and] to $D_s(002)/D_s(100) < 1.2$ and a pan. When it is in this range, it is because it excels in infrared impermeability and antistatic property.

[0019]And when setting to D_w the size of microcrystal for which it asked using the Wilson's method, it is preferred to satisfy $1 \leq D_w \leq 100$ (nm) and the range of it is $5 \leq D_w \leq 30$ (nm) more preferably. If D_w is too small, ultraviolet absorbability, infrared permeability, and antistatic property will fall, and if too large, the transparency over visible light will fall. From a point of infrared impermeability and antistatic property, the one of D_w where microcrystal is larger is preferred, and its smaller one is preferred from a point of a visible light transmittance state. D_w is preferred at the point that the range which is 5-30 nm can balance both performances. When D_w is in said range, it becomes the thing excellent in transparency, infrared interception nature, ultraviolet absorbability, and antistatic property. It is desirable when setting to A_w the lattice strain for which it asked using the Wilson's method, and A_w satisfies $0 \leq A_w \leq 1$ (%). It is the range of $0 \leq A_w \leq 0.5$ (%) more preferably. When A_w is in said range, it thinks because Md contains more monomeric, but infrared interception nature and antistatic property become the highest.

[0020]Morphology in particular, such as form of the zinc oxide system particles used by this invention and particle diameter, is not limited. As an example of form, although thin film integrated circuits, such as a globular shape, an ellipse globular shape, the shape of a cube, rectangular parallelepiped shape, the shape of a pyramid, a

needle, a column, tubed [rod-like], the shape of scaphocerite, and tabular (hexagon head), etc. are illustrated, it is preferred that a microcrystal form is in the above-mentioned range.

[0021]As for the zinc oxide system particles used by this invention, it is preferred to contain the carboxyl residue (carboxylic acid group) of carboxylic acid 0.01 to 10% by the weight ratio to ZnO, and containing 0.1 to 5% is more preferred. Transparency becomes high, when secondary condensation is suppressed and it is considered as a paint in a carboxylic acid group existing in a particle surface. On the other hand, if there are too many carboxylic acid groups, the membranous infrared interception nature and antistatic property which were formed will fall. When the amount of carboxylic acid groups is in said range, it becomes monodisperse nature, antistatic property, and the thing excellent in both infrared cutoff performances. Zinc oxide system particles may contain the carbonic acid group in 3% or less of range preferably 10% or less by the weight ratio to ZnO.

[0022]The zinc oxide system particles used by this invention can be dealt with as a dispersing element distributed in a solvent. This dispersing element contains zinc oxide system particles and a solvent as an essential ingredient. As for zinc oxide system particles, it is preferred to contain at 2 to 80weight % of a rate by the metallic-oxide conversion over a dispersing element total amount. 20 to 60 weight % is especially preferred.

[0023]As a solvent, water, alcohols, ketone, aliphatic series, and aromatic carboxylate. straight mineral oil, vegetable oil, a wax oil, silicone oil, etc. besides ether, ether ester species, aliphatic series and aromatic hydrocarbon, and halogenated hydrocarbon can be mentioned -- these solvents -- one sort -- or two or more sorts are used. . The boiling points [in / in a desirable solvent / ordinary pressure] are 40 ** - 250 ** from a point of flexibility. They are one sort or two sorts or more of mixed solvents chosen from alcohols, aliphatic series and aromatic hydrocarbon, halogenated hydrocarbon, aromatic series and aliphatic-carboxylic-acid ester species, ketone, ether (annular), ether ester species, and water. Methanol, ethanol, n-propanol, isopropyl alcohol, n-butanol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Diethylene glycol monoethyl ether, diethylene-glycol monobutyl ether, Ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, Ethylene glycol butyl ether acetate, propylene glycol monomethyl ether, Propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, Tripropylene glycol monomethyl ether, propylene-glycol-methyl-ether acetate, Propylene glycol ethyl ether acetate, 3-methyl-3-methoxybutanol, 3-methyl-3-methoxy butyl acetate, toluene, xylene, benzene, cyclohexane, n-hexane, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, a tetrahydrofuran, water, The dispersing element which contains at least one sort or two sorts or more of mixed solvents chosen from the group, ** and others, is especially preferred in order to tend to obtain the higher coating composition of dispersibility.

[0024]Next, the manufacturing method of zinc oxide system particles used by this invention is explained. The method of depositing zinc oxide system particles is mentioned by heating Zn compounds, the compound of Md, and the solution (S) that contains the compound of Ma if needed, for example as a manufacturing method of zinc oxide system particles used by this invention. As Zn compounds used with the manufacturing method of zinc oxide system particles, Metal zinc (zinc dust), zinc oxides (flower of zinc etc.), zinc hydroxide, basic zinc carbonate, mono- or di-carboxylate (for example, the zinc acetate.) which may have a substituent Octylic acid

zinc, zinc stearate, oxalic acid zinc Lactic acid zinc, tartaric acid zinc, and zinc naphthenate, At least one chosen from among the groups which consist of organozinc compounds, such as chelate compound of zinc, such as zincky alkoxides (alkyl), beta-diketone, hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, and quinoline, is preferred. When using these Zn compounds, a desalting process becomes unnecessary, and a process decreases compared with the time of using the zinc chloride which needs a desalting process, zinc nitrate, or sulfate of zinc. If these Zn compounds are used, the particles which are excellent in the monodisperse nature which does not have [that it is few or] the content of the impurity H will be obtained. Especially, metal zinc (zinc dust), a zinc oxide (flower of zinc), zinc hydroxide, basic zinc carbonate, and zinc acetate are inexpensive, and their handling is preferred at an easy point. Since a zinc oxide, zinc hydroxide, and zinc acetate moreover tend to control the size and form of a crystal and particles, excluding substantially an impurity which checks the generation reaction of the crystal of the zinc oxide in a heating process, they are still more preferred. The zinc oxide made especially by a gaseous phase method (an French method, the laws of U.S.) is preferred. the zinc oxide of a gaseous phase method can choose arbitrarily the kind of it not only being able to obtain inexpensive but monocarboxylic acid -- in addition, though especially the particles by which form or particle diameter was controlled by using these raw materials are easy to be obtained and the impurity H is included, since it is very small, it is especially desirable.

[0025]As a metal (Md) compound used with a manufacturing method of zinc oxide system particles, For example, metal; oxide; hydroxide, such as a metal simple substance of metal Md, and an alloy; Carbonate, Mineral, such as halogenides, such as a nitrate, sulfate, a chloride, and fluoride; Acetate, Carboxylate, such as propionate, butyrate, and a lauric acid salt; Metal alkoxides;beta-diketone, All the compounds containing metal (Md), such as metal chelate compound with hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, quinoline, etc., are mentioned. In the case of a metallic element in which metal Md can take two or more valences like In and Tl. At least one compound (this compound is a concept also containing metal, such as a metal simple substance and an alloy) chosen from a group which consists of a compound containing metal of a low valence which may change to trivalent or tetravalence eventually in a creation-of-particles process is used. There are few organometallic complexes which do not contain the impurity H like metal of metal Md, an oxide, hydroxide, carbonate (acidity and basic carbonate are included), acetate, an alkoxide compound, and beta-diketone compound in these, or the impurity H has them at a point which is not. [preferred]

[0026]As a metal (Ma) compound used with a manufacturing method of zinc oxide system particles, For example, metal; oxide; hydroxide, such as a metal simple substance of the metal Ma, and an alloy; Carbonate, Mineral, such as halogenides, such as a nitrate, sulfate, a chloride, and fluoride; Acetate, Carboxylate, such as propionate, butyrate, and a lauric acid salt; Metal alkoxides;beta-diketone, All the compounds containing metal (Ma), such as metal chelate compound with hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, quinoline, etc., are mentioned. There are few organometallic complexes which do not contain the impurity H like metal of the metal Ma, an oxide, hydroxide, carbonate (acidity and basic carbonate are included), acetate, an alkoxide compound, and beta-diketone compound in these, or the impurity H has them at a point which is not. [preferred]

[0027]As for a solution (S), it is preferred that a monocarboxylic acid compound and alcohol are included. A monocarboxylic acid compound is a compound which has

only one carboxyl group in intramolecular. As an example of this compound, formic acid, acetic acid, propionic acid, isobutyric acid, Caproic acid, caprylic acid, lauric acid, myristic acid, pulmitic acid, Saturated fatty acid, such as stearic acid (saturation monocarboxylic acid); Acrylic acid, Cyclic saturation monocarboxylic acid, such as unsaturated fatty acid (unsaturation monocarboxylic acid); cyclohexane carboxylic acid, such as methacrylic acid, crotonic acid, oleic acid, and linolenic acid; Benzoic acid, Containing halogen monocarboxylic acid, such as anhydride; trifluoroacetic acid of the above-mentioned monocarboxylic acid, such as aromatic-monocarboxylic-acids; acetic anhydrides, such as phenylacetic acid and toluic acid, monochloroacetic acid, and o-chlorobenzoic acid; it is lactic acid etc. These monocarboxylic acid compounds may be used alone and may be used together two or more.

[0028]A desirable monocarboxylic acid compound is saturated fatty acid which has the boiling point 200 °C or less at 1 atmosphere. Specifically, formic acid, acetic acid, propionic acid, butanoic acid, and isobutyric acid are preferred at a point that particles which are excellent in monodisperse nature are easy to be obtained. As for this saturated fatty acid, it is preferred to use it in the 60-100-mol% of range to a total amount of a monocarboxylic acid compound, and it is more preferred to use it in the 80-100-mol% of range. There is a possibility that the crystallinity of a zinc oxide in particles which will be obtained if less than said range may become low.

[0029]As for a monocarboxylic acid compound, 50 to 200 times are preferred to Md of Md compound at a mole ratio. Eight or less times 1.90 or more-time are preferred at the mole ratio to Zn. It is because the particles which are excellent in monodisperse nature and are excellent in antistatic property when a film is formed, and the grant performance of IR cut performance are easy to be obtained. As alcohol used with the manufacturing method of zinc oxide system particles, aliphatic series monohydric alcohol (methanol, ethanol, and isopropyl alcohol.) n-butanol, t-butyl alcohol, stearyl alcohol, etc., aliphatic series unsaturation monohydric alcohol (allyl alcohol and clo chill alcohol.) alicyclic monohydric alcohol (cyclopentanol.), such as propargyl alcohol aromatic monohydric alcohol (benzyl alcohol.), such as cyclohexanol monohydric alcohol; alkylene glycol [, such as heterocyclic monohydric alcohol,] (furfuryl alcohol etc.) (ethylene glycol.), such as cinnamyl alcohol and methylphenylcarbinol Propylene glycol, a trimethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1, 8-octanediol, 1,10-Decanediol, a pinacol, a diethylene glycol, triethylene glycol, etc., the aliphatic series glycols which have an aromatic ring, and alicyclic glycols (hydrobenzoin, a benzpinacol, phthalyl alcohol, etc.) (cyclopentane 1,2-diol and cyclohexane-1,2-diol.) polyoxy alkylene glycol (a polyethylene glycol.), such as cyclohexane-1,4-diol a polypropylene glycol etc. -- etc. -- glycols; -- propylene glycol monoethyl ether. Propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, Tripropylene glycol monomethyl ether, 3-methyl-3-methoxybutanol, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Derivatives, such as monoether of the above-mentioned glycols, such as triethylene glycol monomethyl ether and ethylene glycol mono- acetate, and monoester; Hydroquinone, Aromaticdiol, these monoether, and monoester, such as resorcinol and 2,2-bis(4-hydroxyphenyl)propane; it is trihydric alcohol and these monoether, monoester, a diether, diester, etc., such as glycerin. these alcohol -- one sort -- or two or more sorts are used.

[0030]As for alcohol, it is preferred to consider it as 1-30 times the amount to zinc oxide equivalent weight of brewing Mino Zn compounds, and it is more preferred to consider it as 15-25 times the amount. As for a mole ratio of alcohol to a monocarboxylic acid compound, it is preferred to consider it as one to 10 times. Zinc

oxide system particles which contain the above Ma(s) in a solution (S) by making a compound of Ma contain in the less than one range by an atomic ratio (Ma/Md) of Ma of Ma compound to Md of Md compound contained in a solution (S) can be obtained easily. By making Ma live together, it is effective in particles which are excellent in monodisperse nature being obtained irrespective of the amount of metal Md (addition ratio to zinc). Zinc oxide system particles made into the purpose under conditions which could lessen quantity of a solvent required in order to obtain a solution (S) containing Md compound and Zn compounds on a process, therefore were excellent in an economic target are obtained.

[0031] From a point of the monodisperse nature of particles obtained, coexistence of Ma changes also with kinds of metal Md, when the amount of metal Md to Zn is high, but. It is effective when Md/Zn (atomic ratio) is not less than 3%, Md is IIIB fellows and IVB fellows, Md is except the above, and Md/Zn (atomic ratio) is 1% or more. as the desirable method of preparation of a solution (S) -- ** -- beforehand Md compound with a solution (Sa) obtained by carrying out the uniform dissolution in a solvent. Liquid (a solution or suspension may be sufficient) containing a zinc compound or a zinc compound is mixed, method ** which obtains a solution (S) containing Md and zinc -- beforehand some of Md compounds and zinc compounds with a solution (Sb) obtained by carrying out the uniform dissolution in a solvent. Liquid (a solution or suspension may be sufficient) containing remaining zinc compound or a zinc compound is mixed, and a method of obtaining a solution (S) containing Md and zinc is mentioned. What is necessary is just to add Ma compound, when preparing Sa from the above-mentioned Reason if needed in **, and preparing Sb in **. In order to obtain the above-mentioned solution (Sa, Sb), it is preferred to heat at temperature which can usually be heated above 50 ** and carries out reflux. As a suitable solvent used by Sa and Sb, one sort or two sorts or more of mixtures, such as monocarboxylic acid mentioned above, an anhydride of this monocarboxylic acid, water, and alcohol mentioned above, are mentioned.

[0032] The dispersion liquid of the particles where crystallite size gathered and which do not have condensation are easy to be obtained by heating a solution (S) at 150-200 ** preferably, and depositing zinc oxide system particles. Further in the bottom of the non-oxidizing atmosphere of 0.1% or less of an oxygen density the atmosphere of a gas portion the obtained dispersion liquid in a well-closed container, By performing heat-treatment of less than 24 hours 1 minute or more at not less than 200 ** the temperature below 400 **, crystallinity is higher and the particles excellent in grant of infrared interception nature when a film is formed, and antistatic property are obtained. By making temperature of heat-treatment into the range of 220-300 **, the particles excellent in especially monodisperse nature can be obtained. Since infrared cutoff performance and antistatic property may fall if it carries out the bottom of an oxidizing atmosphere, it is not desirable.

[0033] An atomic number [as opposed to zinc for the total content of the impurity H in a solution (S)]. (However, in the case of a sulfuric acid root, in the case of the atomic number of S, and a nitric acid root, it calculates as an atomic number of N) By a ratio, by considering it as 0.001% or less 0.01 more% or less 0.1% or less especially more preferably 0.5% or less, Zinc oxide system particles with few above impurities H can be obtained easily. It contains, also when the impurity H is not included at all in a solution (S), of course.

[0034] When a solution (S) contains carbonate in 0.001 to 5% of range by the number ratio of mols of CO₃ to Zn of the Zn compounds contained in a solution (S), the controlled photocatalyst activity particles can also be obtained. By the above process,

$0.5 < D_s(002)/D_s(100) < 1.0$, $5 \leq D_w \leq 30$ (nm), and $0 \leq A_w \leq 0.5$ (%) can be satisfied, and the impurity H can obtain 0.1% or less of particles preferably 0.5% or less by the atomic ratio to zinc. [Binder component] The binder component used by this invention is an ingredient in which the coat which has film formation performance, combines zinc oxide system particles, is excellent in antistatic property, and is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility is made to form. This binder component may contain binder resin as an essential ingredient, and may contain a cross linking agent if needed.

[0035]As binder resin, various synthetic resins (the thermosetting, the ultraviolet curing nature, the electron beam hardenability, moisture curing nature, these concomitant use, etc.), a natural resin, etc. of thermoplasticity or hardenability can be mentioned. As a synthetic resin, for example Alkyd resin, amino resin, polyvinyl resin, An acrylic resin, an epoxy resin, polyamide resin, polyurethane resin, Thermosetting unsaturated polyester resin, phenol resin, chlorinated polyolefin resin, silicone resin, acrylic silicone resin, a fluoro-resin, xylene resin, petroleum resin, ketone resin, rosin denaturation maleic acid resin, liquid polybutadiene, coumarone resin, etc. can be mentioned -- these -- one sort -- or two or more sorts are used. as a natural resin, shellac, rosin (turpentine), rosin ester, hardened rosin, decolorization shellac, white shellac, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0036]As alkyd resin, for example Super-short oil alkyd resin, short oil alkyd resin, Pure alkyd resin, such as middle oil alkyd resin, long oil alkyd resin, and super-long oil alkyd resin; by rosin, phenol, epoxy, styrene, urethane, silicon, amino resin, a natural resin, synthetic resin, a polymerization nature monomer, etc. modified-alkyd-resin; which denaturalized the above-mentioned pure alkyd resin -- oil free alkyd resin containing oil free alkyd resin and the amount of polymers oil free alkyd resin can be mentioned -- these -- one sort -- or two or more sorts are used.

[0037]As amino resin, for example Butylated melamine resin, methylation melamine resin, Melamine resin and melamine formaldehyde resin, such as benzoguanamine resin; Butyl-ized urea resin, urea resin and urea resin; -- the amino alkyd copolycondensation resin etc. which carried out copolycondensation of melamine resin, or urea resin and alkyd resin can be mentioned -- these -- one sort -- or two or more sorts are used. [, such as butyl-ized urea melamine resin,]

[0038]the polymerization nature monomer (vinyl acetate.) of polyvinyl chloride, VCM/PVC, and others as polyvinyl resin Vinyl chloride resin, such as a copolymer with lower-fatty-acid vinyl ester, such as vinyl propionate, a vinylidene chloride, etc.; Polyvinyl acetate, vinyl acetate and other polymerization nature monomers (ethylene, propylene, and styrene.) Vinyl acetate resin, such as a copolymer with acrylic ester, vinyl propionate, a vinylidene chloride, etc.; Polyvinyl alcohol of the saponification degree of several kinds, various denaturation (silicone modification, carboxyl denaturation, and amino modifying -- it and) [epoxy-] Polyvinyl alcohol resin, such as polyvinyl alcohol, such as mercapto denaturation; A polyvinyl butyral, butyral resin (vinyl alcohol, vinyl acetate, etc.) of vinylbutyral and other polymerization nature monomers, such as a copolymer, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0039]A copolymer which uses acrylic acid (meta) and its ester as the main ingredients of a main chain as the above-mentioned acrylic resin, for example; (meta) A copolymer of acrylic ester, Thermoplastic acrylic resins, such as a copolymer of acrylic ester and polymerization nature monomers, such as vinyl system monomers

(styrene, vinyl ester, etc.); (Meta) To a monomer which constitutes a thermoplastic acrylic resin. (Meta) Hydroxy alkyl ester of acrylic acid and acrylic acid (meta), (Meta) Thermosetting acrylics, such as what added a cross linking agent component or heat cure ingredients, such as glycidyl ester of acrylic acid; (meta) Styrene other than an acrylic system monomer, Moisture curing which makes a copolymer component a copolymer which denaturalized by monomers, such as vinyltoluene and vinyl acetate, and an acrylic monomer which has a silyl group (alkoxy silyl groups) of hydrolysis nature is possible, Epoxy curing type acrylic resin in which silicon concentration contained in resin makes a copolymer component an acrylic monomer which has silyl modified resin; basicity nitrogen which is 1 or less weight %, and uses an epoxy compound for a cross linking agent component; An acrylic resin etc. which have an oxidative polymerization function can be mentioned, these -- one sort -- or two or more sorts are used.

[0040]As an epoxy resin, for example A bisphenol A type, a bisphenol female mold, A 2,6-xlenol type, a bromination bisphenol A type, a phenol novolac type, glycidyl ether type [, such as an orthocresolnovolac type,]; -- glycidyl ester type [of synthetic fatty acid, such as dimer acid,]; -- an aromatic amine type (glycidyl amine type) etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0041]A hardening agent may be used together when using an epoxy resin as binder resin. As a hardening agent, for example Polymercaptan, aliphatic polyamine, aromatic polyamine, polyamide, tertiary amine, diethylamino propylamine, imidazole, a tertiary amine salt, alicyclic amine, an acid anhydride, boron fluoride and amine salt, dicyandiamide, polyphenol, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0042]As polyurethane resin, for example An oil denaturation type, a moisture curing type, a heat cure type, 1 liquid type polyurethane resin [, such as a lacquer type,]; -- a polyol hardening type (acrylic polyol.) various polyols, such as polyester polyol and polyether polyol, and an isocyanate prepolymer should put together -- two-component type polyurethane resin, such as a catalyst hardening type, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0043]As phenol resin, for example Resol type phenol resin and novolac type phenol resin, what denaturalized these phenol resin with an epoxy resin, alkyd resin, polyvinyl butyral resin, polyamide, an acrylic resin, drying oil, rosin, petroleum resin, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0044]as chlorinated polyolefins, chlorinated polyethylene resin, chlorinated polypropylene resin, chlorinated rubber, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As silicone resin (organopolysiloxane), the straight-silicone-resin; alkyd denaturation of for example, dimethyl silicone, methylphenyl silicone, etc., epoxy denaturation, polyester denaturation, acrylic modification, the denaturation silicone resin by which urethane denaturation was carried out, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0045]as for acrylic silicone resin, the silicon concentration contained in resin is 1 weight % or more of a thing, for example, silicon concentration can mention 1 weight % or more of an alkoxy-silyl-groups content acrylic copolymer etc. -- these -- one sort -- or two or more sorts are used. As a fluoro-resin, for example Polyvinyl fluoride, polyvinylidene fluoride, A chlorotrifluoroethylene copolymer, a tetrafluoroethylene hexafluoropropylene copolymer, Thermoplastic fluoro-resins, such as an ethylene chlorotrifluoroethylene copolymer and a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer; Fluoro olefins, such as tetrafluoroethylene, alkyl vinyl ether, hydroxyalkyl vinyl ether, Solvent meltable type fluoro-resins, such as an alternating copolymer

(FEVE resin) with vinyl ether, such as carboxy alkyl vinyl ether; A vinylidene fluoride hexafluoropropylene copolymer, A tetrafluoroethylene propylene copolymer, fluorine-containing silicone series fluorocarbon rubber, Fluorine-containing vinyl ether system fluorocarbon rubber, fluorine-containing phosphazene system fluorocarbon rubber, fluorocarbon rubber [, such as a fluorine-containing thermoplastics elastomer]; -- other fluorocarbon rubbers, such as a fluorine-containing epoxy resin, fluorine-containing polyimide, and fluorine-containing silicone, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0046]Water and/or an organic solvent are distributed or a thermoplastic fluoro-resin is used with the form of a granular material, although there are some which are not dissolved in a solvent. The solvent meltable type fluoro-resin which introduced bridge construction ingredients, such as hydroxyl, can be hardened by an isocyanate or melamine resin. as xylene resin, denaturation xylene resin, such as native xylene resin; phenol denaturation and rosin denaturation, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0047]as petroleum resin, petroleum resin of petroleum resin; carbon number 5 system of carbon number 9 system, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As a synthetic resin, the rubber of nature, such as ethylene-propylene copolymerization rubber, polybutadiene rubber, a styrene butadiene rubber, and acrylonitrile butadiene copolymerization rubber, or composition, etc. may be used. As an ingredient used together with a synthetic resin, a cellulose nitrate, cellulose acetate butylate, cellulose acetate, ethyl cellulose, hydroxypropylmethylcellulose, hydroxyethyl cellulose, etc. can be mentioned.

[0048]About the form of the binder resin used for an antistatic coating constituent, there is no limitation in particular and a solvent meltable type, a water soluble type, an emulsion type, distributed type (arbitrary solvents, such as water/organic solvent), etc. can be mentioned. As binder resin of a water soluble type, water-soluble alkyd resin, water-soluble acrylic modification alkyd resin, water-soluble oil free alkyd resin (water-soluble-polyester resin), water soluble acrylic resin, water-soluble epoxy ester resin, water-soluble melamine resin, etc. can be mentioned, for example.

[0049]As emulsion type binder resin, for example An alkyl acrylate (meta) copolymerization dispersion; vinyl-acetate-resin emulsion, A vinyl acetate copolymerization resin emulsion, an ethylene-vinyl acetate copolymerization resin emulsion, An acrylic ester (**) polymerization resin emulsion, a styrene acrylic ester (**) polymerization resin emulsion, an epoxy resin emulsion, a urethane resin emulsion, an acrylic silicone emulsion, a fluoro-resin emulsion, etc. can be mentioned.

[0050]When using the antistatic coating constituent of this invention for manufacture of the below-mentioned antistatic film, etc., from a viewpoint of film formation conditions, such as forming temperature, the flexibility of the film obtained, or weatherability, polyurethane resin, an acrylic resin, a fluoro-resin, etc. are preferred as binder resin. As a cross linking agent used as a binder component, For example, the cross linking agent used for drying oil systems, such as air (oxygen); Polyester resin, such as an unsaturated monomer of monofunctional or many organic functions, The cross linking agent used for a poly acrylic resin and an epoxy resin; The 1st class, polyamine containing the 2nd class amino group, The cross linking agent used for the binder resin which has epoxy groups, such as polyamide, the amino resin which has a methylol group and the polybasic acid which has a carboxyl group, and high acid number polyester; The polyisocyanate which has an isocyanate group, The amino group of the polyisocyanate which has a urethane group, a methylol group, the 1st

class, and/or the 2nd class, The cross linking agent used for the binder resin which has carboxyl groups, such as a cross linking agent; metal chelator used for the binder resin which has hydroxyl groups, such as amino resin which has an alkoxy methylene group; Moisture, the cross linking agent etc. which are used for the binder resin which has silicone groups, such as a polyfunctional epoxy compound and hydroxyl group-containing compound, can be mentioned -- these -- one sort -- or two or more sorts are used.

[0051]As a polyisocyanate of the above-mentioned cross linking agents, For example, bird RENJISHISO cyanate, 4, and 4'-diphenylmethane diisocyanate, Hexamethylene di-isocyanate, naphthylene-1,5-diisocyanate, Diisocyanate, such as isophorone diisocyanate and dicyclohexyl methane-4,4'-diisocyanate; The adduct of tolylene diisocyanate and trimethylolpropane, The adduct of hexamethylene di-isocyanate and trimethylolpropane, The trimethylolpropane adduct of isophorone diisocyanate and the above-mentioned diisocyanate, such as an adduct of trimethylolpropane; Isocyanurate denaturation tolylene diisocyanate, Isocyanurate denaturation hexamethylene di-isocyanate, isocyanurate denaturation thing [of the above-mentioned diisocyanate, such as isocyanurate denaturation isophorone diisocyanate,]; -- biuret denaturation thing [of the above-mentioned diisocyanate, such as biuret denaturation hexamethylene di-isocyanate]; -- the above-mentioned diisocyanate and a trimethylolpropane adduct. An isocyanurate denaturation thing, a biuret denaturation thing, etc. Prepolymer-izing, the polymer-ized denaturation thing; above-mentioned diisocyanate, a trimethylolpropane adduct, The isocyanate group in an isocyanurate denaturation thing, a biuret denaturation thing, prepolymer-izing, and the polymer-ized denaturation thing Alcohols, the block-type polyisocyanate etc. which were protected with phenols, oxime, an active methylene compound, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[An antistatic coating constituent and a paint article] An antistatic coating constituent concerning this invention is a constituent which uses the above-mentioned zinc oxide system particles and a binder component as an essential ingredient.

[0052]Although there is no limitation in particular about a rate over total solids of a binder component of zinc oxide system particles, and the zinc oxide system particle total quantity, it is 60 to 80 weight % still more preferably 50 to 95weight % preferably. At this time, hardening agents, such as a cross linking agent, shall also be included in a binder component. There is a possibility that transparency and antistatic property may fall that a rate of zinc oxide system particles is less than 50 weight % to said total-solids total quantity. On the other hand, when a rate of zinc oxide system particles exceeds 95 weight %, there is a possibility that optical properties, such as transparency and colorlessness, endurance, weatherability, adhesion, and flexibility may fall. Especially about weatherability, when a rate of zinc oxide system particles exceeds 80 weight %, it may fall rapidly. In order to solve this problem, it is preferred that silane coupling agent treatment, said M-X group content polymer processing, etc. carry out a surface modification to zinc oxide system particles beforehand, but a manufacturing cost of zinc oxide system particles may rise, and it may be necessary to improve a binder component.

[0053]Without reducing antistatic property as the antistatic coating constituent of this invention is what contains a conductive adjuvant further, the content of zinc oxide system particles can be reduced and, moreover, the weatherability of the coat obtained from an antistatic coating constituent, adhesion, flexibility, endurance, etc. can be raised. It is thought that antistatic property does not fall because a conductive adjuvant carries out the role of ***** which connects zinc oxide system particles and

antistatic efficiency increases even if it reduces the content of zinc oxide system particles, when a conductive adjuvant is included.

[0054]As a conductive adjuvant used by this invention, what at least a part of the surface becomes from conductive substances, such as metal, conductive metallic oxide, and a conductive organic matter, is preferred. The conductive coat adjuvant which should just have covered at least a part of below-mentioned core material with the conductive substance by the surface consisting of conductive substances at least may be sufficient as a conductive adjuvant. as metal used for a conductive adjuvant, alloys, such as metal simple substance; stainless steel, such as iron, nickel, copper, tin, aluminum, lead, zinc, and silver, copper and a zinc alloy, copper, a tin alloy, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0055]as conductive metallic oxide used for a conductive adjuvant, a zinc oxide, Sb dope tin oxide, aluminum dope zinc oxide, Sn dope indium oxide, stannic acid cadmium, rhenium oxide, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As a conductive organic matter used for a conductive adjuvant, For example, Polyacethylene (dopants, such as iodine.) What was doped. it contains --; polypyrrole (dopants, such as periodic acid ion.) What was doped. it contains --; polythiophene (dopants, such as periodic acid ion.) What was doped. it contains -- polythiophenes, such as; poly aniline (what doped dopants, such as EMERARUJIN base, is included); poly para-phenylene (what doped dopants, such as AsF₅, is included); polyphenylene vinylene; polyalkylthio Foehn, heterocyclic content polymer [, such as polypyrrole,]; -- conductive polymers, such as a derivative produced by introducing an ester group, an alkyl group, etc. into aromatic ring content polymer, such as poly para-phenylene, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0056]As a core material which constitutes a conductive coat adjuvant, for example White mica, phlogopite, Nature, such as lepidolite, sericite, and fluoride phlogopite, or synthetic mica, sepiolite (argillite), Kaolinite, talc, bentonite, montmorillonite, a smectite, Organic fiber, such as nature, such as pyrophyllite, or synthetic argillite, nylon, polyester, potassium titanate, boric acid aluminum, titanium oxide, silicon carbide, ferric oxide, a zinc ferrite, a magnesium ferrite, glass, silica, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0057]As a conductive substance used for covering at least a part of core material, the conductive metallic oxide which uses Sn, In, Zn, Sb, and Cd as the metal main ingredients can be mentioned, and it is colorless, or there is little coloring. Although there is no limitation in particular about a conductive adjuvant and the form of a core material, a globular shape, an ellipse globular shape, the shape of a cube, rectangular parallelepiped shape, the shape of a pyramid, tabular, rod form, etc. can be mentioned. Since the probability of contacting zinc oxide system particles among these as they are form of anisotropy with a comparatively large aspect ratio and large surface area, such as tabular and rod form, increases, zinc oxide system particles are connected and antistatic efficiency increases, it is desirable.

[0058]As what is easy to come to hand and it is easy to distribute in the coating composition of this invention as a conductive adjuvant, For example, metal or alloy fibers, such as iron, nickel, copper, aluminum, lead, zinc, and stainless steel, The conductive adjuvant of metal systems, such as scale-like silver and grape-like nickel; The letter tin-oxide particles of a needlelike Sb dope, The conductive adjuvant of conductive-metallic-oxide systems, such as tetrapod-like zinc oxide particles; Sb dope tin-oxide covering potassium titanate whisker, Conductive coat adjuvants, such as Sb dope tin-oxide covering boric acid aluminum whisker, Sb dope tin-oxide covering

titanium oxide whisker, Sb dope tin-oxide covering mica, and polypyrrole covering polyester fiber, etc. can be mentioned.

[0059]When the conductive adjuvants used by this invention are tabular particles, there is no limitation in particular about thickness t , but 0.008-0.5-micrometer 0.005-1 micrometer [0.008-0.1-micrometer] is 0.008-0.05 micrometer still more preferably preferably. There is a possibility that the mechanical strength of tabular particles may fall that thickness t is less than 0.005 micrometer, and endurance may fall. On the other hand, when thickness t exceeds 1 micrometer, there is a possibility that transparency may fall. Although there is no limitation in particular also about length [of tabular particles] L , 0.05-20-micrometer 0.02-50 micrometers are 0.1-5 micrometers most preferably still more preferably. There is a possibility that antistatic property may fall that length L is less than 0.02 micrometer. On the other hand, when length L exceeds 50 micrometers, there is a possibility that endurance, adhesion, and flexibility may fall. the aspect ratio (L/t) of tabular particles -- desirable -- 2-500 -- further -- desirable -- 4-100 -- it is 6-50 most preferably.

[0060]The form of a board (projected type from a top) may be arbitrary, and tabular [as used in the field of this invention] may be form including circular, an ellipse, a spindle shape, a triangle, a quadrangle, a rhombus, a hexagon, an octagon, an infinite form, etc., and may be the shape of a piece, a thin film integrated circuit, the shape of a scale, hexagon-head tabular, etc., for example. When the conductive adjuvant used by this invention is a rod-like particle, there is no limitation in particular about the thickness d (the maximum thickness which passes along the center of a rod-like particle), but. 0.008-0.5-micrometer 0.005-1 micrometer [0.008-0.1-micrometer] is 0.008-0.05 micrometer still more preferably preferably. There is a possibility that the mechanical strength of a rod-like particle may fall that the thickness d is less than 0.005 micrometer, and endurance may fall. On the other hand, when the thickness d exceeds 1 micrometer, there is a possibility that transparency may fall. Although there is no limitation in particular also about length [of a rod-like particle] L , 0.05-20-micrometer 0.02-50 micrometers are 0.1-5 micrometers most preferably still more preferably. There is a possibility that antistatic property may fall that length L is less than 0.02 micrometer. On the other hand, when length L exceeds 50 micrometers, there is a possibility that endurance, adhesion, and flexibility may fall. the aspect ratio (L/t) of a rod-like particle -- desirable -- 2-500 -- further -- desirable -- 4-100 -- it is 6-50 most preferably.

[0061]The rod form as used in the field of this invention is form including a needle, filar, fibrous, whisker shape, the shape of a strip of paper, the shape of a star, tubular, a line, the arborescence for which two or more these gathered, the shape of a grape, etc. Conductive adjuvants may be other form particles other than tabular particles and a rod-like particle. In addition, as form particles, the particles of polyhedron shape, such as a globular shape, the shape of *****, the shape of a spindle body, the shape of a tetrahedron, the shape of hexahedron, the shape of octahedron, and the shape of a dodecahedron, etc. can be mentioned, for example. In addition, 3 axis pitch diameter of form particles $[(L+b+t) / 3]$ is 0.05-2 micrometers still more preferably preferably. [0.005-10-micrometer]

[0062]When the antistatic coating constituent of this invention contains a conductive adjuvant with zinc oxide system particles and a binder component, Although there is no limitation in particular about the rate (a 100x conductivity adjuvant / zinc oxide system particles) over the zinc oxide system particles of a conductive adjuvant, it is 0.5 to 3 weight % most preferably 0.3 to 5weight % still more preferably 0.1 to 20weight %. There is a possibility that antistatic property may fall that the rate over

the zinc oxide system particles of a conductive adjuvant is less than 0.1 weight %. On the other hand, when the rate of a conductive adjuvant exceeds 20 weight %, there is a possibility that endurance, adhesion, and flexibility may fall.

[0063]When the antistatic coating constituent of this invention contains a conductive adjuvant, about the rate over the solid content of a binder component of a conductive adjuvant, and the zinc oxide system particle total quantity. Although there is no limitation in particular, it is 0.25 to 1.5 weight % most preferably 0.25 to 5 weight % still more preferably 0.05 to 9.5 weight %. There is a possibility that antistatic property may fall that the rate over said total quantity of a conductive adjuvant is less than 0.05 weight %. On the other hand, when the rate over said total quantity of a conductive adjuvant exceeds 9.5 weight %, there is a possibility that transparency, endurance, adhesion, and flexibility may fall.

[0064]The antistatic coating constituent of this invention may contain a solvent, and is suitably chosen by the kind of binder component, etc. As a solvent, for example Alcohols, aliphatic series, and aromatic carboxylic acid ester. organic system solvent; water; straight-mineral-oil; vegetable oil, such as ketone, ether, ether ester species, aliphatic series and aromatic hydrocarbon, and halogenated hydrocarbon, a wax oil, silicone oil, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0065]The antistatic coating constituent of this invention in addition to zinc oxide system particles, a binder component, and a conductive adjuvant, According to a military requirement, Hardening agent [, such as a cross linking agent,];. Curing catalyst; of a hardening auxiliary agent etc. plasticizer; -- defoaming agent and leveling agent; -- thixotropic agent; -- flattening; -- surface-active agent; -- fire retardant; -- paints wetting agent and dispersing agent; -- lubricant; -- ultraviolet ray absorbent; - light stabilizer; -- antioxidant; -- in addition to this (heat) -- stabilizer; -- antiseptic; - antifungal agent; -- seaweed-proofing agent; -- corrosion prevention and rust-preventives; -- color; -- additive agents, such as paints, may be contained.

[0066]The hardening agent used for drying oil systems, such as air (oxygen), as the above-mentioned hardening agent, for example; Polyester resin, such as an unsaturated monomer of monofunctional or many organic functions, The hardening agent used for a poly acrylic resin and an epoxy resin; The 1st class, polyamine containing the 2nd class amino group, The hardening agent used for the resinous principle which has epoxy groups, such as polyamide, the amino resin which has a methylol group and the polybasic acid which has a carboxyl group, and high acid number polyester; The polyisocyanate which has an isocyanate group, The amino group of the polyisocyanate which has a urethane group, a methylol group, the 1st class, and/or the 2nd class, The hardening agent used for the resinous principle which has carboxyl groups, such as a hardening agent; metal chelator used for the resinous principle which has hydroxyl groups, such as amino resin which has an alkoxy methylene group; Moisture, the hardening agent etc. which are used for the resinous principle which has silicone groups, such as a polyfunctional epoxy compound and hydroxyl group-containing compound, can be mentioned -- these -- one sort -- or two or more sorts are used.

[0067]As a polyisocyanate of the hardening agents, For example, bird RENJISHISO cyanate, 4, and 4'-diphenylmethane diisocyanate, Hexamethylene di-isocyanate, naphthylene-1,5-diisocyanate, Diisocyanate, such as isophorone diisocyanate and dicyclohexyl methane-4,4'-diisocyanate; The adduct of tolylene diisocyanate and trimethylolpropane, The adduct of hexamethylene di-isocyanate and trimethylolpropane, The trimethylolpropane adduct of isophorone diisocyanate and the above-mentioned diisocyanate, such as an adduct of trimethylolpropane;

Isocyanurate denaturation tolylene diisocyanate, Isocyanurate denaturation hexamethylene di-isocyanate, isocyanurate denaturation thing [of the above-mentioned diisocyanate, such as isocyanurate denaturation isophorone diisocyanate,]; -- biuret denaturation thing [of the above-mentioned diisocyanate, such as biuret denaturation hexamethylene di-isocyanate]; -- the above-mentioned diisocyanate and a trimethylolpropane adduct. An isocyanurate denaturation thing, a biuret denaturation thing, etc. Prepolymer-izing, the polymer-ized denaturation thing; above-mentioned diisocyanate, a trimethylolpropane adduct, The isocyanate group in an isocyanurate denaturation thing, a biuret denaturation thing, prepolymer-izing, and the polymer-ized denaturation thing Alcohols, the block-type polyisocyanate etc. which were protected with phenols, oxime, an active methylene compound, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0068]As a curing catalyst, for example Zinc naphthenate, calcium naphthenate, A curing catalyst used for drying oil systems, such as metal driers, such as an octylic acid zirconium, and an organic dryer; A redox system initiator, Polyester resin, such as a sensitizer (ultraviolet rays, an electron beam, etc. are required), a poly acrylic resin, A curing catalyst used for an epoxy resin; Amines and metallic compounds (heat is required), A hardening agent used for binder resin which has hydroxyl groups, such as organic acid (heat is required) and inorganic acid (heat may be necessity); A curing catalyst etc. which are used for binder resin which has silicone groups, such as metallic compounds and amines (humidity and heat are required), can be mentioned, these -- one sort -- or two or more sorts are used.

[0069]As a plasticizer, for example Dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, phthalic acid benzyl butyl ester, diisodecyl phthalate, tricresyl phosphate, diphenyl phosphate KUREJIRU, triphenyl phosphate dibutyl sebacate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0070]As a defoaming agent and a leveling agent, for example An acrylic defoaming agent, an acrylic leveling agent, a vinyl system defoaming agent, a vinyl system leveling agent, a silicone series defoaming agent, a silicone series leveling agent, a mineral system defoaming agent, a thixotropic agent (a thickening agent, an antissettling agent, a dripping inhibitor), etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0071]About the form of a thixotropic agent, there is no limitation in particular and the thixotropic agent for solvent systems, the thixotropic agent for drainage systems, etc. can be mentioned. As a thixotropic agent for solvent systems, for example An organic bentonite system, Thixotropic agents for inorganic particle system solvent systems, such as a superfines silica system and a surface treatment calcium carbonate system; An AMAIDO wax system, a hydrogenation castor oil wax system, a benzyliene sorbitol system, and metallic soap (zinc stearate.) An oxidation polyethylene system, such as aluminum stearate, a polymerization vegetable oil system, thixotropic agents for organic system solvent systems, such as a sulfate ester system anionic surface active agent system, a polyether ester type surfactant system, and a polycarboxylic acid amine salt system, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0072]as the thixotropic agent for drainage systems -- thixotropic agents for inorganic particle system water, such as for example, a superfines silica system and a magnesium aluminium silicate system, --; xanthan gum. thixotropic agents for organic system water, such as a guar gum, a sodium-polyacrylate system, acrylic acid and an acrylic ester copolymer system, a polyvinyl alcohol system, a polyethylene oxide system, and a urethane denaturation polyether system, etc. can be mentioned -- these -

- one sort -- or two or more sorts are used.

[0073]as a flattening, hydrous silicon dioxides, such as white carbon, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as a surface-active agent -- for example, the Nonion system (a polyethylene-glycol type.) anionic systems (a sulfate ester type and a sulfonic acid type.), such as a polyhydric alcohol type a carboxylic type, a phosphoric ester type, etc. can mention surface-active agents (an amine acid type, a betaine type, etc.) of cation systems (an amine salt type, quarternary ammonium salt, etc.) and a both sexes system, etc. -- these -- one sort -- or two or more sorts are used.

[0074]as fire retardant, an antimony trioxide, aluminium hydroxide, a chlorinated paraffin, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as a paints wetting agent and a dispersing agent, a paints wetting agent and a dispersing agent for solvent systems, a paints wetting agent, a dispersing agent for drainage systems, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0075]As a paints wetting agent and a dispersing agent for solvent systems, for example The amount unsaturation polycarboxylic acid of polymers, Polyether polyester carboxylate, the amount polyester acid polyamine salt of polymers, Polycarboxylic acid salt, AMAIDO amine salt of the amount polyester acid of polymers, long chain polyamino AMAI drine compounds acid, A salt of aliphatic series poly AMAIDO, long chain polyamino AMAIDO, and polymer polyester acid, The various amount compounds of polymers, such as a polymer polyether system compound; Phosphoric ester, cationic compounds, such as salts of anionic compound; fatty amines, such as phosphate, fatty alcohol sulfuric ester salt, sulfonated oil, and alkyl-sulfonic-acid salts, and quarternary ammonium salt, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0076]As the paints wetting agent and a dispersing agent for water, for example The salt of the amount polycarboxylic acid of polymers, The salt of styrene maleic acid copolymer, the formalin condensate of naphthalene sulfonic acid, the salt of long chain alkyl organic sulfonic acid, the salt of ligninsulfonic acid, the salt of polyphosphoric acid and poly silicic acid, a long chain alkylamine salt, a polyethylene glycol derivative, a sorbitan fatty acid ester, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0077]as lubricant, aliphatic hydrocarbon system lubricant, high-class aliphatic series system alcohol and higher-fatty-acid system lubricant, fatty acid AMAIDO system lubricant, metallic soap system lubricant, fatty-acid-ester system lubricant, compound lubricant, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as an ultraviolet ray absorbent, ultraviolet ray absorbents, such as a benzophenone series, a benzotriazol system, an oxalic acid anilide system, a cyanoacrylate system, and a triazine series, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0078]As the above-mentioned light stabilizer, for example Bis(1,2,2,6,6-pentamethyl 4-piperidyl)sebacate, hindered amine light stabilisers, such as methyl 1,2,2,6,6-pentamethyl 4-piperidyl sebacate and bis(2, 2, 6, and 6-tetramethyl 1-octyloxy 4-piperidyl)Deccan dioate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0079]as the above-mentioned antioxidant -- a phenol system (a mono- phenol system.) sulfur-compounds systems (dilauryl thiodipropionate.), such as a bisphenol system and a polymer system dimyristyl thiodipropionate etc. can mention phosphorus-compounds systems (a triphenyl boss fin, diphenyl isodecyl phosphate,

etc.) etc. -- these -- one sort -- or two or more sorts are used.

[0080]in addition -- (heat) as stabilizer, tin series stabilizer, lead system stabilizer, stearic acid system stabilizer, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As tin series stabilizer, for example A di-n-octyltin bis(isooctylthio glycolic acid ester)salt, Di-n-octyltin maleate polymer, a di-n-octyl SUZUJI lauric acid salt, Di-n-octyl tin series stabilizer, such as a di-n-octyltin ester maleate salt; A di-n-butyl tinbisma lane acid ester salt, Malete series compounds, such as a di-n-butyl tin ester maleate salt, a di-n-butyl SUZUBISU octylthio glycol ester salt, Mercapto system compounds, such as di-n-butyl tin beta-mercaptopropionic acid salt polymer, di-n-butyl tin series stabilizer [, such as laurate system compounds, such as di-n-butyl tin dilaurate,]; -- dimethyl tin series stabilizer, such as a dimethyltin bis(isooctylmercapto acetate)salt, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0081]as lead system stabilizer, 3 basicity lead sulfate, 2 basicity lead stearate, 2 basicity phosphorous acid lead, lead stearate, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As stearic acid system stabilizer, for example Barium stearate, calcium stearate, magnesium stearate, aluminum stearate, lithium stearate, 12-hydroxylithium stearate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0082]In addition (heat) as stabilizer, may use stabilizer other than the above-mentioned tin series stabilizer, lead system stabilizer, and stearic acid system stabilizer, and as such stabilizer, For example, behenic acid lithium, myristic acid lithium, triphenyl phosphite, diphenyl isodecyl phosphite, tris nonylphenyl phosphite, barium zinc liquefied compound stabilizer, calcium zinc liquefied compound stabilizer, cadmium barium zinc liquefied compound stabilizer, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0083]As an antiseptic, an antifungal agent, and a seaweed-proofing agent, for example 1,2-benziso thiazoline 3-one, 5-chloro-2-methyl-4-iso thiazoline 3-one, a p-chloro-m-xyleneol, 2-hydroxy methylamino ethanol, etc. can be mentioned -- these -- one sort -- or two or more sorts are used. as corrosion prevention and rust preventives, ethylamines and propylamine can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0084]Weatherability of the antistatic coating constituent of this invention improves that it is what contains light stabilizer further. About the curing method of an antistatic coating constituent, a heat cure method is economically preferred. Although there is no limitation in particular about the manufacturing method of the antistatic coating constituent of this invention, the metaphor can mix a binder component to the dispersing element containing zinc oxide system particles, and can mention the method of mixing a conductive adjuvant further, etc. to it suitably.

[0085]The paint article concerning this invention forms in a base material surface the coat obtained from the above-mentioned antistatic coating constituent. Since this paint article equips that surface with the coat obtained from an antistatic coating constituent, it has the outstanding antistatic property and the weatherability of a coat, adhesion, and flexibility are high. As a base material, base materials, such as inorganic substances, such as glass and earthenware, and organic matters, such as resin, can be mentioned, especially the coat produced by applying an antistatic coating constituent to the base material surface of an organic matter has high weatherability, and it excels in flexibility, for example. About the form of the above-mentioned inorganic substance or an organic matter, there is no limitation in particular and form, such as film state, a sheet shaped, tabular, and fibrous, can be mentioned. Also among

these, it is useful for the below-mentioned film, fiber, etc.

[0086] There is no limitation in particular as construction material of the resin used as a base material. For example, LDPE, HDPE, amorphous polyethylene, OPP (extension polypropylene), Polypropylene, such as CPP (crystallization polypropylene), Polyolefin systems, such as polyisobutylene; EVA. (Ethylene-vinyl acetate copolymer) system; -- polystyrene system; -- elasticity or rigid-polyvinyl-chloride; -- EVOH (ethylene vinyl alcohol copolymer) system; P VA system (nylon system); P VDC system (polyvinylidene chloride); -- polyethylene terephthalate and polyethylenenaphthalate. Polyester system [, such as polybutylene naphthalate,]; polycarbonate system; -- polyurethane system; -- polyamide system; -- polyimide system; -- polyacrylonitrile system; -- Pori Sall John system; -- polyether sulphone system; -- polyphenylene sulfide system; -- polyarylate system; -- polyether imide system; -- aramid system; (meta-) acrylic; -- polyether ether ketone system; -- a tetrafluoroethylene ethylene copolymer, a tetrafluoroethylene hexafluoropropylene copolymer, polytetrafluoroethylene, polytrifluoroethylene, polyvinylidene fluoride, and polyvinyl fluoride. A tetrafluoroethylene perfluoro-alkyl vinyl ether copolymer, Fluororesin, such as polyvinyl fluoride, a tetrafluoroethylene hexafluoropropylene perfluoro-alkyl vinyl ether copolymer, and polychlorotrifluoroethylene resin, etc. can be mentioned.

[0087] In using for the use as which the very advanced visible light transmittance state of an optical lens etc. and transparency are required, A PMMA and MMA-styrene random copolymer, polycarbonate, Copolymers, such as transparent polypropylene, MMA, alpha-methylstyrene, or cyclohexyl methacrylate, The MMA denaturation type of ABS plastics, polystyrene, polyarylate, Pori Sall John, Various resin, such as polyether sulphone, transparent-epoxy-resin, Poly 4-methylpentene- 1, fluorinated polyimide, amorphous-fluorocarbon-resin, transparent phenoxy resin, and amorphous nylon resin and a fluorene series, can be used as a base material.

[0088] It becomes more important future still to use biodegradable resin as a base material from a disposal treatment problem as what meets the demand to biodegradability. For example, in such a case, Poly 3-hydroxy butylate, It is preferred to use biodegradable plastics, such as a kitchen chitosan system, a polyamino acid system, a cellulose type, a polycaprolactone system, an alginic acid system, a polyvinyl alcohol system, an aliphatic polyester system, a sugars system, a polyurethane system, and a polyether system, etc. as a base material.

[0089] It may be the purpose of improving the adhesion etc. of what arranged UV absorption film on the above-mentioned base material beforehand, and the coat and base material which are obtained from an antistatic coating constituent as a base material, and the thing thing which allotted the primer layer etc. beforehand may be used. Fluororesin, polyester system resin, acrylic (meta) resin, and polycarbonate system resin are preferred at the point that weatherability is high among a plastic film and a sheet also about the inside of these resin used as a base material.

[0090] The paint article of this invention can be manufactured by making the above-mentioned base material surface apply and harden an antistatic coating constituent, for example. About the method of applying an antistatic coating constituent to a base material surface, there is no limitation in particular and a dipping method, the roll coater method, the flow coat method, screen printing, the bar coating-machine method, the spin coater method, brush painting, a spray method, etc. can be mentioned.

[0091] After applying an antistatic coating constituent, in order to raise physical properties, such as chemical resistance, such as a water resisting property, solvent

resistance, acid-proof, and alkali-proof, and abrasion-proof nature, it is preferred to make it harden by methods, such as heat curing (room temperature curing is included), moisture curing, ultraviolet curing, and electron beam hardening. There is no limitation in particular about the dry membrane thickness of the coat obtained from an antistatic coating constituent, and 0.2-5-micrometer 0.5-50 micrometers are 0.5-2 micrometers most preferably still more preferably.

[0092] Although there is no limitation in particular about the surface resistance ρ of the coat obtained from an antistatic coating constituent, below $10^9 \Omega/\square$ are [below $10^{10} \Omega/\square$] $10^6 - 10^9 \Omega/\square$ most preferably still more preferably.

Although there is no limitation in particular about Hayes of the coat obtained from an antistatic coating constituent, it is 1% or less most preferably 2% or less still more preferably 5% or less. Hayes is the value produced by measuring with a turbidity meter.

[0093]

[Working example] Although the embodiment of this invention is shown together with a comparative example below, in addition, this invention is not limited to the following embodiment. A "part" and a "weight section" are shown in the following embodiments. Evaluation in this example was performed with the following technique.

1. The addition metal content of the evaluation <particle presentation> powder sample of zinc oxide system particles, other metal contents, and impurity H content were calculated by X-ray fluorescence, atomic absorption analysis, plasma emission spectrometry, gravimetric analysis, ultimate analysis, etc.

The <crystalline> powder X diffraction estimated. The passage of the following [valuation basis / crystalline].

[0094]

O There is a diffraction peak of :ZnO crystal.

x: There is no diffraction peak of a ZnO crystal.

It asked by performing powder X diffraction measurement of the <crystallite diameter D_s (hkl), D_w , and lattice strain A_w > powder sample.

By the D_s (hkl):Scherrer method (based on the Cauchy approximation of function).

The size of microcrystal and 1 g of lattice strain <carboxylic acid group content> powder samples for which it asked using the crystallite diameter D_w of a vertical direction and the A_w :Wilson method from each diffracting plane (hkl) obtained are mixed in the sodium hydroxide solution of 0.01N, After stirring for three days, it measured by conducting ion chromatograph analysis of the supernatant fluid obtained by centrifugation operation.

By carrying out vacuum drying of a part of <particle concentration of dispersing element> dispersing element until it can remove volatile constituents, such as a solvent, thoroughly in 100 **, obtain the end of dried powder and a retained material when this is heated at 500 ** among the air for 1 hour is used as a metallic oxide, It asked for a weight fraction to a dispersing element for a metallic oxide, and this value was made into particle concentration (metallic-oxide conversion concentration) in a dispersing element.

2. To an evaluation <surface resistance> paint film surface of a coat obtained from an antistatic coating constituent. The golden Kushigata electrode was vapor-deposited (thickness 30nm**5nm), after neglecting it for 12 hours under a temperature-and-humidity condition shown in a table, and protection-from-light conditions, electrometer 617 type by KESURE was used and a surface resistance value under the conditions was measured (impressed electromotive force 0.1 V). Measurement of

surface resistance was performed by the measuring condition (1) and (2) shown in a table.

[0095] Surface resistance of a coat after an accelerated weathering test did an accelerated weathering test on JIS B 7753-93 for 200 hours using sunshine carbon arc light type lightfastness and a weather meter of a description, and measured subsequent surface resistance. Surface resistance after a water resistant test was immersed in boiling water of pure water for 10 hours, and measured subsequent surface resistance. With a <light transparency and transparency> turbidity meter (Nippon Denshoku Industries Co., Ltd. make NDH-1001 DP), the total light transmittance T and Hayes H were measured.

The transparency after a <transparent endurance> accelerated weathering test did the accelerated weathering test on JIS B 7753-93 for 200 hours using the sunshine carbon arc light type lightfastness and the weather meter of a description, and measured it after that. Using the turbidity meter (the Nippon Denshoku Industries Co., Ltd. make, NDH-1001 DP), measurement of transparency was asked for difference $\Delta H(\%) = H - H_0$ of initial haze value H_0 and haze value H after an examination, and it judged by the following valuation basis to it. The passage of the following [valuation basis / of transparency].

[0096]

The particle system analyzer according [the dispersibility of the zinc oxide system particles in the evaluation <dispersibility> antistatic coating constituent of an H< 10% of H< 5% of of H< 1% of AA: $\Delta A:1\% \leq \Delta B:5\% \leq \Delta C:10\% \leq \Delta H3$. antistatic coating constituent, etc.] to a dynamic-light-scattering system (Nozaki& Co., Ltd. NICOMP.) Using Model370, it asked for the mean particle diameter of the weight reference, and this was made into the mean-dispersion particle diameter Dd. The passage of the following [valuation basis / of dispersibility]. However, in the system which adds a cross linking agent and a curing catalyst, dispersibility was measured, before adding these.

[0097]

A: $Dd \leq 30nm$ B : the appearance of the dispersing element after settling a $\leq 50nm$ C: $50nm < Dd \leq 100nm$ D: $100nm < Dd$ <dispersion-stability> antistatic coating constituent on the degree of bath temperature of 50 ** for 30 days in the state where it was immersed in the organ bath, 30 nm<Dd was evaluated. The passage of the following [valuation basis / of a dispersion stability].

[0098]

A: The state which does not carry out layer separation and does not have sediment.

B: Although there is sediment, carry out re dispersion by shake.

C: Sediment, even if it shakes, don't carry out re dispersion but gel.

When manufacturing a <pot-life> antistatic coating constituent, after adding a cross linking agent, it stirred at 20 ** and membranes were formed for every hour. About the obtained coat, transparency and hardenability were investigated and the maximum T of the mixing time in which these physical properties do not get worse was measured, respectively. The passage of the following [valuation basis / of pot life].

[0099]

A: The cotton which made $T > 6\text{-hour}$ B: $6\text{-hour} \geq T > 3\text{-hour}$ C: $T \leq 3\text{-hour}$ <hardenability> methyl ethyl ketone impregnate was ground 100 times on the coat, and the rubbing test was done. The surface state of the coat after a test was observed. The passage of the following [valuation basis / of hardenability].

[0100]

O : with no change.

** : A crack is seen on the surface.

x: A coat dissolves.

About the <adhesion> coat, the squares friction test by a cellophane tape was done, and adhesion was investigated. The passage of the following [valuation basis / of adhesion].

[0101]

A: 100/100 (completely with no exfoliation)

Bending was performed 3 less than [less than / less than / B: / 80/100 or more / 100/100C: / 50/100 or more / 80/100D:] 50/100 <flexibility> 90 degrees, and the crack generated on the surface and the existence of exfoliation were observed with the microscope. The passage of the following [valuation basis / flexible].

[0102]O : with no change.

** : Although exfoliation is not carried out, a crack occurs.

x: Exfoliate.

- Without carrying out the surface modification of the zinc oxide system particles P1 of the physical properties shown in the embodiment 1(1)-table 1, toluene was distributed and the dispersing element D1 (50 weight % of particle concentration) was prepared. To this dispersing element D1, the binder B1 grade shown in Table 3 was mixed by the combination shown below, it stirred at 25 ** to it for 3 hours, and the antistatic coating constituent C1 was obtained to it. The physical properties of the antistatic coating constituent C1 are shown in Table 5.

[0103]

Dispersing element D1 (50 weight % of particle concentration) 40 weight section Binder B1 (35% of nonvolatile matter concentration) 14.3 weight section Leveling agent (polysiloxane system) 0.05 weight section The antistatic coating constituent C1 obtained by the toluene 35 weight-section above. After applying by Bar Goh Tarr on the surface of the PET film and carrying out hot air drying for 2 minutes at 80 **, it was recuperated for three days at 50 **, and the coat (1) of 0.5 micrometer of dry membrane thickness was obtained. The various physical properties of a coat (1) are evaluated and the result is shown in Table 7.

[0104]- The surface modification which shows the zinc oxide system particles P2-P5 of the physical properties shown in Embodiment 1 (2) - the 1(7)-table 1 in Table 2 was performed, the solvent shown in Table 2 was distributed, and the dispersing elements D2-D5 were prepared. To these dispersing elements D2-D5, mixed addition of binder B-2 shown in Table 3 - the B7 grade was carried out by the combination shown in Table 4, respectively, and the antistatic coating constituents C2-C7 were obtained like Embodiment 1 (1). The physical properties of the antistatic coating constituents C2-C7 are shown in Table 5.

[0105]

[Table 1]

酸化亜鉛系粒子	添加金属含有量 (Zn基準)		粉末X線解析結果			結晶性	不純物H含有量 (Zn基準) モル%	他金属含有量 (Zn基準)		カルボン酸基含有量 重量%
	Md	モル%	Dw nm	Ds比 002/100	Aw %			金属	モル%	
P1	Al	1	20	0.79	0.10	○	<0.001	0		3.1
P2	In	4	12	0.60	0.01	○	<0.001	Na	0.1	0.5
P3	Ga	2.5	15	0.89	0.10	○	<0.001	Li	0.3	0.9
P4	Y	0.5	30	0.90	0.22	○	<0.001	Mg	0.2	4.3
P5	Hf	0.9	18	0.93	0.22	○	<0.001	0		2.4
P6	Ga	2.0	22	1.29	0.28	○	Cl:1.09	0		<0.001

[0106]

[Table 2]

酸化 亜鉛 系粒 子	表面修飾剤	処理量	分 散 体	分散体組成	
		(酸化亜鉛系粒子基準) 重量%		粒子濃度 酸化物換算*1 重量%	溶媒
P 1	なし	—	D 1	5 0	トルエン
P 2	重合体A*2	1 0 . 0	D 2	4 0	トルエン
P 3	カルボキシル変性ポリメチルシロキサン	1 . 0	D 3	4 0	酢酸ブチル
P 4	アクリルアセートアルミニウムソノゾロレート	2 . 4	D 4	2 0	酢酸ブチル
P 5	ヒドロキシエチルトリメチシラン	1 8	D 5	3 0	イソブタノール
P 6	なし	—	D 6	1 0	トルエン

*1: 600℃焼成時の灰分重量から求めた。

*2: 重合体Aは、メタクリレート(20部)、シロキシメタクリレート(75部)およびメタクリルオキシトリメチシラン(5部)を重合して得られた重合体

[0107]

[Table 3]

バインダー種類		備 考			
		酸価	数平均 分子量	OHV	
B 1	アクリル樹脂	0.5	30,000	-	HALSハイブリッドタイプ
B 2	アクリル樹脂	2	6,000	40	HALSハイブリッドタイプ
B 3	フッ素樹脂	2.5	10,000	24	
B 4	ポリウレタン樹脂 (ポリエステルポリオール)	8	3,000	250	
B 5	水溶性アクリル樹脂	pH 8	-	-	アミン中和タイプ
B 6	アクリルシリコン樹脂	-	12,000	-	Si-OCH ₃ 基含有
B 7	紫外線硬化型 ウレタンアクリレート	0.1	-	-	

[0108]

[Table 4]

実施例1	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	主溶媒	他の添加剤
(1)	C1	D1	B1	なし	2.8	7.8	トルエン	レベリング剤
(2)	C2	D2	B2	架橋剤A*3	4.5	7.3	トルエン	レベリング剤
(3)	C3	D2	B3	架橋剤A*3	3.5	8.0	トルエン	レベリング剤
(4)	C4	D4	B4	架橋剤A*3	5.0	8.0	酢酸ブチル	—
(5)	C5	D5	B5	なし	5.0	7.7	イソブチルアルコール	—
(6)	C6	D5	B6	なし	3.0	7.0	イソブチルアルコール	ジブチルスラウレート
(7)	C7	D3	B7	なし	6.0	8.2	酢酸ブチル	—

* 1 : 600℃焼成時の灰分重量から求めた酸化物換算濃度。

* 2 : 固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

* 3 : 架橋剤Aは、イソシアレート変性ヘキサメチレンジイソシアネートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアネート基がモル比で、1 : 1となるように添加した。

[0109]

[Table 5]

	帯電防止塗料組成物	塗膜	帯電防止塗料組成物物性			塗膜物性		
			分散性	分散安定性	ポットライフ	硬化性	密着性	可撓性
実施例 1 (1)	C1	(1)	A	A	A	×	B	○
実施例 1 (2)	C2	(2)	A	A	A	○	A	○
実施例 1 (3)	C3	(3)	A	A	B	○	A	○
実施例 1 (4)	C4	(4)	B	B	B	○	A	—
実施例 1 (5)	C5	(5)	B	B	A	△	B	—
実施例 1 (6)	C6	(6)	A	B	B	○	B	—
実施例 1 (7)	C7	(7)	A	B	A	○	A	○
比較例 1	C11	(11)	D	B	A	○	D	△

[0110]The antistatic coating constituents C2-C7 were formed on the conditions shown in Table 6, respectively, and the coat (2) - the coat (7) were obtained. The film formation condition which obtains a coat (1) from the antistatic coating constituent C1 was also shown in Table 6. The acquired physical properties of a coat (2) - a coat (7) are evaluated, and the result is shown in Table 7.

[0111]

[Table 6]

実施例1	塗膜	帯電防止塗料組成物	基材	乾燥条件	膜厚 ドライ μm
(1)	(1)	C1	PET7μm	80℃、2分間	0.5
(2)	(2)	C2	PET7μm	100℃、2分間	1
(3)	(3)	C3	フッ素7μm	100℃、2分間	3
(4)	(4)	C4	PMMA板	60℃、1時間	6
(5)	(5)	C5	ガラス	80℃、5分間	3
(6)	(6)	C6	PC板	常温、1カ月	5
(7)	(7)	C7	PET7μm	*1	1

*1：高圧水銀灯（80W/cm）、距離15cmで、5秒間

[0112]

[Table 7]

実施例1	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性 T H (%) (%)		透明耐 久性 促進耐 候性試 験後
		環境条件 (1)	環境条件 (2)	環境条件 (1)				
				促進耐候 性試験後	耐水試験 後			
(1)	(1)	4.4X10 ⁷	3.9X10 ⁷	8.0X10 ⁷	7.1X10 ⁷	86	3.3	A
(2)	(2)	8.7X10 ⁷	8.0X10 ⁷	9.0X10 ⁷	8.8X10 ⁷	87	2.5	AA
(3)	(3)	1.9X10 ⁸	2.0X10 ⁸	1.9X10 ⁸	1.8X10 ⁸	92	3.0	AA
(4)	(4)	3.2X10 ⁸	3.2X10 ⁸	3.5X10 ⁸	3.3X10 ⁸	89	1.0	A
(5)	(5)	7.1X10 ⁸	6.8X10 ⁸	>10 ¹⁰	>10 ¹⁰	88	0.8	C剥離
(6)	(6)	1.0X10 ⁹	9.9X10 ⁷	4.0X10 ⁸	3.2X10 ⁸	87	2.4	B
(7)	(7)	3.5X10 ⁸	3.1X10 ⁸	3.6X10 ⁸	3.6X10 ⁸	87	2.7	A

環境条件 (1) : 10℃、相対湿度20%

環境条件 (2) : 30℃、相対湿度60%

[0113]- In the dispersing element D1 (50 weight % of particle concentration) and binder B1 grade which were used in embodiment 2(1)-embodiment 1 (1). The whisker

shape particle powder (the thing in which the antimony content tin-oxide film was formed on the titania whisker surface, length:2micrometer, a diameter: 0.1-micrometer and aspect ratio:20) as a conductive adjuvant was added, and the antistatic coating constituent C8 of the presentation shown in Table 8 was prepared. The coat (8) was obtained by the film formation condition which shows the antistatic coating constituent C8 in Table 9. The physical properties of the obtained coat (8) are evaluated and the result is shown in Table 10.

[0114]- To the dispersing element D2, binder B-2, etc. which were used in embodiment 2(2)-embodiment 1 (2). The whisker shape particle powder (the thing in which the antimony content tin-oxide film was formed on the boric-acid aluminum whisker surface, length:18micrometer, a diameter: 0.8-micrometer and aspect ratio:20) as a conductive adjuvant was added, and the antistatic coating constituent C9 of the presentation shown in Table 8 was prepared. The coat (9) was obtained by the film formation condition which shows the antistatic coating constituent C9 in Table 9. The physical properties of the obtained coat (9) are evaluated and the result is shown in Table 10.

[0115]- In the dispersing element D2 and binder B3 grade which were used in embodiment 2(3)-embodiment 1 (2). The whisker shape particle powder (an antimony dope tin-oxide whisker, length:2.0micrometer, a diameter: 0.01-micrometer and aspect ratio:200) as a conductive adjuvant was added, and the antistatic coating constituent C10 of the presentation shown in Table 8 was prepared. The coat (10) was obtained by the film formation condition which shows the antistatic coating constituent C10 in Table 9. The physical properties of the obtained coat (10) are evaluated and the result is shown in Table 10.

[0116]- The antistatic coating constituent C11 was prepared like Embodiment 1 (1) except using the particles P6 of the physical properties shown in Table 1 instead of the zinc oxide system particles P1 used in comparative example 1-embodiment 1 (1). The physical properties of the antistatic coating constituent C11 are shown in Table 5. The antistatic coating constituent C11 was formed to the PET film like Embodiment 1 (1), and the coat (11) was obtained. The physical properties of the obtained coat (11) are evaluated and the result is shown in Table 10.

[0117]

[Table 8]

実施例2	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	導電性補助剤**/酸化亜鉛系粒子 重量%	主溶媒	他の添加剤
(1)	C8	D1	B1	なし	28	75	1	トルエン	レベリング剤
(2)	C9	D2	B2	架橋剤A**	25	65	2	トルエン	レベリング剤
(3)	C10	D2	B3	架橋剤A**	55	70	4	トルエン	レベリング剤

*1：600℃焼成時の灰分重量から求めた酸化物換算濃度。

*2：固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

*3：導電性補助剤として、実施例2（1）～2（3）に記載したウィスカー状粒子粉末を用いた。

*4：架橋剤Aは、イソシアレート変性ヘキサメチレンジイソシアネートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアネート基がモル比で、1：1となるように添加した。

[0118]

[Table 9]

実施例2	塗膜	帯電防止塗料組成物	基材	乾燥条件	膜厚 ドライ μm
(1)	(8)	C8	PETフィルム	80℃、2分間	0.5
(2)	(9)	C9	PETフィルム	100℃、2分間	1
(3)	(10)	C10	フッ素フィルム	100℃、2分間	3

[0119]

[Table 10]

	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性		透明耐 久性
		環境条件 (1)	環境条件 (2)	環境条件 (1)				
				促進耐候 性試験後	耐水試験 後	T (%)	H (%)	促進耐 候性試 験後
実施例 2 (1)	(8)	8.8X10 ⁶	8.4X10 ⁶	9.0X10 ⁶	8.8X10 ⁶	85	3.8	A
実施例 2 (2)	(9)	2.2X10 ⁷	2.0X10 ⁷	3.0X10 ⁷	2.8X10 ⁶	84	4.2	AA
実施例 2 (3)	(10)	3.0X10 ⁶	2.8X10 ⁶	3.7X10 ⁶	3.9X10 ⁶	88	3.6	AA
比較例 1	(11)	1.2X10 ⁷	1.3X10 ⁷	—	—	82	22	C

環境条件 (1) : 10℃、相対湿度 20%

環境条件 (2) : 30℃、相対湿度 60%

[0120]

[Effect of the Invention] The antistatic coating constituent concerning this invention has a low dependency over humidity, temperature, etc., has the antistatic property stable for a long period of time, and can form the coat which is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility. The coat which the paint article concerning this invention has the antistatic property stable for a long period of time, and was formed in the surface has optical properties, such as transparency and colorlessness, endurance, adhesion, and high flexibility.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to an antistatic coating constituent and its use.

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PRIOR ART

[Description of the Prior Art]Conventionally, as an antistatic coating constituent, the paint which contains the surface-active agent of metal particle; anionic systems, such as conductive-metallic-oxide particle; copper, such as a zinc oxide system and a tin oxide system, and nickel, a cation system, and both sexes, etc. as a spray for preventing static electricity is known. Among these, with the constituent containing particles, such as a metallic oxide and metal, the particle diameter of particles was large, or since the dispersibility in the inside of a paint and a coat was insufficient, it excelled in transparency, and the antistatic film without coloring was not obtained. In order to give antistatic property, it is necessary to include many particles in a paint, and it cannot be satisfied, even if neither the flexibility of a coat, nor adhesion, weatherability which are obtained are enough and use a coat as an antistatic film. [0003]Environment dependency, such as the antistatic property under low humidity being insufficient, and being on the other hand, based on a transmission machine style peculiar to a surface-active agent, although the coat which is excellent in transparency is obtained in the paint which contains a surface-active agent as a spray for preventing static electricity, was high. Since the weatherability of the surface-active agent which is a spray for preventing static electricity was low, the endurance of the coat was not enough, when long term use was carried out, the coat deteriorated and there were various problems with practical coloring arising, or a surface-active agent carrying out bleeding, and antistatic performances falling, or blocking arising etc.

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EFFECT OF THE INVENTION

[Effect of the Invention]The antistatic coating constituent concerning this invention has a low dependency over humidity, temperature, etc., has the antistatic property stable for a long period of time, and can form the coat which is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility. The coat which the paint article concerning this invention has the antistatic property stable for a long period of time, and was formed in the surface has optical properties, such as transparency and colorlessness, endurance, adhesion, and high flexibility.

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TECHNICAL PROBLEM

[Problem to be solved by the invention]The issue which this invention tends to solve is providing the antistatic coating constituent which can form the coat which the dependency over humidity, temperature, etc. is low, has the antistatic property stable for a long period of time, and is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility, and its use.

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MEANS

[Means for solving problem]The binder component in which the antistatic coating constituent concerning this invention has film formation performance, In the antistatic coating constituent containing the zinc oxide system particles which use as a metallic component the metallic element (Md) and Zn which take trivalent and/or tetravalence, and show zinc oxide crystal nature in X diffraction study, The ion and/or atom of a halogen excluding [said zinc oxide system particle] F, an atomic number [as opposed to zinc in the total content of the impurity H which consists of sulfuric acid root SO_4^{2-} and nitric acid root NO_3^-] (however, in the case of a sulfuric acid root, in the case of the atomic number of S, and a nitric acid root, it calculates as an atomic number of N) -- the antistatic coating constituent characterized by what is been 0.5% or less in a ratio.

[0006]When a diffraction peak with said zinc oxide system particle peculiar to a crystalline zinc oxide appears and it asks for the size $D_s(hkl)$ of vertical microcrystal from two lattice planes (100) and (002) using the Scherrer method (Cauchy approximation of function), When setting to D_w the size of microcrystal which

satisfied $D_s(002)/D_s(100) < 2$ and for which it asked using the Wilson's method, it is $1 \leq D_w \leq 100$ (nm).

It is preferred that they are the zinc oxide system particles to satisfy.

[0007] As for this antistatic coating constituent, it is preferred that a conductive adjuvant is included further. The paint article concerning this invention is a paint article which forms the coat obtained from the above-mentioned antistatic coating constituent on the surface of a base material.

[0008]

[Mode for carrying out the invention] Below, first, after explaining zinc oxide system particles, a binder component is explained and, finally the antistatic coating constituent and paint article of this invention are explained.

[Zinc oxide system particles] Their dependency over humidity, temperature, etc. is low, and the zinc oxide system particles used by this invention show the antistatic property stable for a long period of time while they show infrared impermeability, conductivity, etc. in addition to the original ultraviolet-rays cover nature of zinc oxide system particles, and a visible light transmittance state.

[0009] Zinc oxide system particles use as a metallic component the metallic element (Md) and Zn which take trivalent and/or tetravalence. The content of Md is expressed with the ratio of the atomic number of Md to the total atomic number of this metallic component, and it is preferred that it is 0.1 to 20%, and it is 3 to 8% still more preferably 1 to 10% more preferably. If less [if it exceeds said range, it will be hard to become the particles which are rich in homogeneity, such as a presentation and a crystal size, and] than said range, infrared cover nature including a heat ray will become insufficient, and antistatic property will fall.

[0010] As Md which is an alloying element, B, aluminum, Ga, In, Tl, C, Si, Ti, Zr, Sc and Y, Hf besides IIIB group elements, such as germanium, Sn, and Pb, and an IVB group element, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Rv, Os, Rh, Ir, La, Ce, Sb, etc. are mentioned. The zinc oxide system particles used by this invention need to show zinc oxide crystal nature in X diffraction study.

[0011] It is the point of excelling in the permeability over the light of a visible light wavelength region, and infrared interception nature as particle diameter of the primary particle of zinc oxide system particles, It is preferred that the crystallite diameter D_w for which it asked using the Wilson's method (the Wilson method) is 1-50 nm (0.001-0.05 micrometer), and it is preferred to distribute without these primary particles condensing the 2nd order. As for the distributed particle diameter D_d of zinc oxide system particles, it is preferred that it is 1 micrometer or less from the point, i.e., the point which improve transparency and gives optical properties, such as colorlessness, of not affecting substantially the hue of the constituent obtained when a transparent feeling is high and adds to a constituent. 0.5 micrometer or less is 0.1 micrometer or less still more preferably more preferably. Especially 0.05 micrometer or less is preferred. It is preferred that points, such as transparency, adhesion, and weatherability, to monodisperse nature is high. monodisperse nature -- a ratio with the crystallite diameters D_w and D_d -- it defines as $R (D_d/D_w)$, it is preferred that R is ten or less, it is more preferred that it is three or less, and 1.5 especially or less are preferred.

[0012] Distributed particle diameter is the mean particle diameter of the weight reference which can be measured by dynamic light scattering, a centrifuge, etc. In the case of 0.1 micrometers or more, the former measuring method is measured by the latter measuring method at the case below 0.1 micrometer. As zinc oxide system particles used by this invention, polymer constitutes a matrix, the thing (polymer

composite particles) of the form which particles are distributing in this matrix is also contained, and it excels that it is hollow shape in optical diffusional permeability. Although the content in particular of the zinc oxide system particles in this particle is not limited, it is desirable that it is 50 to 95weight % of a range to the complex particle whole quantity in zinc oxide conversion.

[0013]As polymer used for composite-ization, acrylic resin system polymer, alkyd resin system polymer, Amino resin system polymer, polyvinyl resin system polymer, epoxy resin system polymer, Polyamide resin system polymer, polyimide resin system polymer, polyurethane resin system polymer, Polyester resin system polymer, phenol resin system polymer, organopolysiloxane system polymer, The others which are acrylic-silicone-resin system polymer, a polyalkylene glycol, etc., Polyolefin system polymer, such as polyethylene and polypropylene, polystyrene system polymer, Thermoplasticity or thermosetting resin, such as a fluoro-resin system; synthetic rubbers, such as ethylene-propylene copolymerization rubber, polybutadiene rubber, and an acrylonitrile butadiene rubber, crude rubber; polysiloxane group content polymer, etc. can be mentioned.

[0014]As form of a complex particle, as for the surface of a complex particle, although there is no limitation in particular, it is preferred that it is rich in unevenness nature. When unevenness is shown in the surface, it is because compatibility with a binder component etc. becomes high in the coat containing a complex particle. Especially as mean particle diameter of a complex particle, although not limited, it is usually the range of 0.001-10 micrometers. Zinc oxide system particles have a preferred thing which are the purposes, such as weatherability grant by photocatalyst activity reduction with compatibility with the binder component which has the below-mentioned film formation ability, the dispersibility in the inside of an antistatic coating constituent, a dispersion stability, and a zinc oxide, and it comes to process by a surface modification agent.

[0015]Although the above mentioned polymer can also be used as a desirable surface modification agent, the compound containing a M-X basis is mentioned from the purpose of weatherability grant. However, X is at least one sort chosen from a hydrogen atom, a halogen atom, and OR^1 , R^1 is at least one sort chosen from the group which consists of a hydrogen atom, the alkyl group which may be replaced, a cycloalkyl group, an aryl group, an aralkyl group, and an acyl group, and at least one sort of M chosen from a metallic element and the group which consists of Si, Ti, Zr, and aluminum especially is preferred. From a viewpoint of grant of dispersibility (dispersibility to a paint or a solvent, stability of a paint, etc.), the polymer which has an organic high polymer chain is mentioned. It is polymer which a thing desirable by both sides of weatherability and dispersibility contains a M-X basis, and has an organic high polymer chain, for example, polysiloxane group content polymer, acrylic silicone, etc. are mentioned.

[0016]As for zinc oxide system particles, it is preferred that are an atomic ratio of Ma to Md and the univalent or divalent metallic element Ma is included in $0.00001 \leq Ma/Md < 1$. It is more preferred that it is the range of $0.0001 \leq Ma/Md \leq 0.4$. It is preferred that it is 0.0001 to 2% of range at the atomic ratio to zinc. The existence effect of Ma makes Md contain homogeneously during a ZnO crystal (in monomeric state), moreover stabilizes a crystal surface, and is at the point which controls secondary condensation and crystal growth. Therefore, it becomes a detailed high crystal of monodisperse nature. Therefore, it also becomes possible to raise antistatic property and infrared cover nature, increasing the amount of Md and excelling in transparency. Although it is indicated by JP,H8-253317,A that existence of an

alkaline metal and alkaline-earth metals is not preferred (the 5th page 7th column lines 40-47), the above effects are done so by containing positively in a mentioned range. If there are too few amounts of Ma(s), an effect will not be revealed, and if there are too many amounts of Ma(s), the weatherability of the coat containing these particles may fall. In the univalent or divalent metallic element Ma, it is an alkali metal and/or an alkali earth metal element, and lithium, sodium, potassium, a rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, etc. are mentioned.

[0017]The halogen (.) excluding [the zinc oxide system particles used by this invention] F Namely, the ion and/or atom of the chlorine Cl, the bromine Br, and iodine I, an atomic number [as opposed to zinc in the total content of sulfuric acid root SO_4^{2-} and nitric acid root NO_3^- (impurity H)] (however, in the case of a sulfuric acid root, in the case of the atomic number of S, and a nitric acid root, it calculates as an atomic number of N) -- it is important that it is 0.5% or less in a ratio. It is 0.001% or less especially preferably 0.01% or less still more preferably 0.1% or less more preferably. Also when the impurity H is not included at all, it contains in this. Only when the impurity H is not contained, or it contains and it does not exceed this range, it becomes the particles excellent in monodisperse nature, and the coat excellent in adhesion or weatherability can be formed as well as transparency.

[0018]The zinc oxide system particles used by this invention are preferred in it being a thing which is a diffraction peak peculiar to a crystalline zinc oxide and which shows a diffraction peak to a lattice plane (100), (002), and (101), and fills the following microcrystal parameters. When it asks for the size Ds (hkl) of vertical microcrystal from each diffracting plane (hkl) using the Scherrer method (the Scherrer method) (Cauchy approximation of function), i.e., the Cauchy approximation of function, $\text{Ds}(002)/\text{Ds}(100) < 2$ is satisfied. It is $0.5 < \text{Ds}(002)/\text{Ds}(100) < 1.0$ preferably [it is more desirable and] to $\text{Ds}(002)/\text{Ds}(100) < 1.2$ and a pan. When it is in this range, it is because it excels in infrared impermeability and antistatic property.

[0019]And when setting to Dw the size of microcrystal for which it asked using the Wilson's method, it is preferred to satisfy $1 \leq \text{Dw} \leq 100$ (nm) and the range of it is $5 \leq \text{Dw} \leq 30$ (nm) more preferably. If Dw is too small, ultraviolet absorbability, infrared permeability, and antistatic property will fall, and if too large, the transparency over visible light will fall. From a point of infrared impermeability and antistatic property, the one of Dw where microcrystal is larger is preferred, and its smaller one is preferred from a point of a visible light transmittance state. Dw is preferred at the point that the range which is 5-30 nm can balance both performances. When Dw is in said range, it becomes the thing excellent in transparency, infrared interception nature, ultraviolet absorbability, and antistatic property. It is desirable when setting to Aw the lattice strain for which it asked using the Wilson's method, and Aw satisfies $0 \leq \text{Aw} \leq 1$ (%). It is the range of $0 \leq \text{Aw} \leq 0.5$ (%) more preferably. When Aw is in said range, it thinks because Md contains more monomeric, but infrared interception nature and antistatic property become the highest.

[0020]Morphology in particular, such as form of the zinc oxide system particles used by this invention and particle diameter, is not limited. As an example of form, although thin film integrated circuits, such as a globular shape, an ellipse globular shape, the shape of a cube, rectangular parallelepiped shape, the shape of a pyramid, a needle, a column, tubed [rod-like], the shape of scaphocerite, and tabular (hexagon head), etc. are illustrated, it is preferred that a microcrystal form is in the above-mentioned range.

[0021]As for the zinc oxide system particles used by this invention, it is preferred to contain the carboxyl residue (carboxylic acid group) of carboxylic acid 0.01 to 10% by the weight ratio to ZnO, and containing 0.1 to 5% is more preferred. Transparency becomes high, when secondary condensation is suppressed and it is considered as a paint in a carboxylic acid group existing in a particle surface. On the other hand, if there are too many carboxylic acid groups, the membranous infrared interception nature and antistatic property which were formed will fall. When the amount of carboxylic acid groups is in said range, it becomes monodisperse nature, antistatic property, and the thing excellent in both infrared cutoff performances. Zinc oxide system particles may contain the carbonic acid group in 3% or less of range preferably 10% or less by the weight ratio to ZnO.

[0022]The zinc oxide system particles used by this invention can be dealt with as a dispersing element distributed in a solvent. This dispersing element contains zinc oxide system particles and a solvent as an essential ingredient. As for zinc oxide system particles, it is preferred to contain at 2 to 80weight % of a rate by the metallic-oxide conversion over a dispersing element total amount. 20 to 60 weight % is especially preferred.

[0023]As a solvent, water, alcohols, ketone, aliphatic series, and aromatic carboxylate. straight mineral oil, vegetable oil, a wax oil, silicone oil, etc. besides ether, ether ester species, aliphatic series and aromatic hydrocarbon, and halogenated hydrocarbon can be mentioned -- these solvents -- one sort -- or two or more sorts are used. . The boiling points [in / in a desirable solvent / ordinary pressure] are 40 ** - 250 ** from a point of flexibility. They are one sort or two sorts or more of mixed solvents chosen from alcohols, aliphatic series and aromatic hydrocarbon, halogenated hydrocarbon, aromatic series and aliphatic-carboxylic-acid ester species, ketone, ether (annular), ether ester species, and water. Methanol, ethanol, n-propanol, isopropyl alcohol, n-butanol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Diethylene glycol monoethyl ether, diethylene-glycol monobutyl ether, Ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, Ethylene glycol butyl ether acetate, propylene glycol monomethyl ether, Propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, Tripropylene glycol monomethyl ether, propylene-glycol-methyl-ether acetate, Propylene glycol ethyl ether acetate, 3-methyl-3-methoxybutanol, 3-methyl-3-methoxy butyl acetate, toluene, xylene, benzene, cyclohexane, n-hexane, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, a tetrahydrofuran, water, The dispersing element which contains at least one sort or two sorts or more of mixed solvents chosen from the group, ** and others, is especially preferred in order to tend to obtain the higher coating composition of dispersibility.

[0024]Next, the manufacturing method of zinc oxide system particles used by this invention is explained. The method of depositing zinc oxide system particles is mentioned by heating Zn compounds, the compound of Md, and the solution (S) that contains the compound of Ma if needed, for example as a manufacturing method of zinc oxide system particles used by this invention. As Zn compounds used with the manufacturing method of zinc oxide system particles, Metal zinc (zinc dust), zinc oxides (flower of zinc etc.), zinc hydroxide, basic zinc carbonate, mono- or di-carboxylate (for example, the zinc acetate.) which may have a substituent Octylic acid zinc, zinc stearate, oxalic acid zinc Lactic acid zinc, tartaric acid zinc, and zinc naphthenate, At least one chosen from among the groups which consist of organozinc compounds, such as chelate compound of zinc, such as zincky alkoxides (alkyl), beta-

diketone, hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, and quinoline, is preferred. When using these Zn compounds, a desalting process becomes unnecessary, and a process decreases compared with the time of using the zinc chloride which needs a desalting process, zinc nitrate, or sulfate of zinc. If these Zn compounds are used, the particles which are excellent in the monodisperse nature which does not have [that it is few or] the content of the impurity H will be obtained. Especially, metal zinc (zinc dust), a zinc oxide (flower of zinc), zinc hydroxide, basic zinc carbonate, and zinc acetate are inexpensive, and their handling is preferred at an easy point. Since a zinc oxide, zinc hydroxide, and zinc acetate moreover tend to control the size and form of a crystal and particles, excluding substantially an impurity which checks the generation reaction of the crystal of the zinc oxide in a heating process, they are still more preferred. The zinc oxide made especially by a gaseous phase method (an French method, the laws of U.S.) is preferred. the zinc oxide of a gaseous phase method can choose arbitrarily the kind of it not only being able to obtain inexpensive but monocarboxylic acid -- in addition, though especially the particles by which form or particle diameter was controlled by using these raw materials are easy to be obtained and the impurity H is included, since it is very small, it is especially desirable.

[0025]As a metal (Md) compound used with the manufacturing method of zinc oxide system particles, For example, metal; oxide; hydroxide, such as a metal simple substance of metal Md, and an alloy; Carbonate, Mineral, such as halogenides, such as a nitrate, sulfate, a chloride, and fluoride; Acetate, Carboxylate, such as propionate, butyrate, and a lauric acid salt; Metal alkoxides; beta-diketone, All the compounds containing metal (Md), such as metal chelate compound with hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, quinoline, etc., are mentioned. In the case of the metallic element in which metal Md can take two or more valences like In and Tl. At least one compound (this compound is a concept also containing metal, such as a metal simple substance and an alloy) chosen from the group which consists of a compound containing the metal of a low valence which may change to trivalent or tetravalence eventually in a creation-of-particles process is used. There are few organometallic complexes which do not contain the impurity H like the metal of metal Md, an oxide, hydroxide, carbonate (acidity and basic carbonate are included), acetate, an alkoxide compound, and beta-diketone compound in these, or the impurity H has them at the point which is not. [preferred]

[0026]As a metal (Ma) compound used with the manufacturing method of zinc oxide system particles, For example, metal; oxide; hydroxide, such as a metal simple substance of the metal Ma, and an alloy; Carbonate, Mineral, such as halogenides, such as a nitrate, sulfate, a chloride, and fluoride; Acetate, Carboxylate, such as propionate, butyrate, and a lauric acid salt; Metal alkoxides; beta-diketone, All the compounds containing metal (Ma), such as metal chelate compound with hydroxycarboxylic acid, ketoester, keto alcohol, amino alcohol, a glycol, quinoline, etc., are mentioned. There are few organometallic complexes which do not contain the impurity H like the metal of the metal Ma, an oxide, hydroxide, carbonate (acidity and basic carbonate are included), acetate, an alkoxide compound, and beta-diketone compound in these, or the impurity H has them at the point which is not. [preferred]

[0027]As for a solution (S), it is preferred that a monocarboxylic acid compound and alcohol are included. A monocarboxylic acid compound is a compound which has only one carboxyl group in intramolecular. As an example of this compound, formic acid, acetic acid, propionic acid, isobutyric acid, Caproic acid, caprylic acid, lauric acid, myristic acid, pulmitic acid, Saturated fatty acid, such as stearic acid (saturation

monocarboxylic acid); Acrylic acid, Cyclic saturation monocarboxylic acid, such as unsaturated fatty acid (unsaturation monocarboxylic acid); cyclohexane carboxylic acid, such as methacrylic acid, crotonic acid, oleic acid, and linolenic acid; Benzoic acid, Containing halogen monocarboxylic acid, such as anhydride; trifluoroacetic acid of the above-mentioned monocarboxylic acid, such as aromatic-monocarboxylic-acids; acetic anhydrides, such as phenylacetic acid and toluic acid, monochloroacetic acid, and o-chlorobenzoic acid; it is lactic acid etc. These monocarboxylic acid compounds may be used alone and may be used together two or more.

[0028]A desirable monocarboxylic acid compound is saturated fatty acid which has the boiling point 200 °C or less at 1 atmosphere. Specifically, formic acid, acetic acid, propionic acid, butanoic acid, and isobutyric acid are preferred at the point that the particles which are excellent in monodisperse nature are easy to be obtained. As for this saturated fatty acid, it is preferred to use it in the 60-100-mol% of range to the total amount of a monocarboxylic acid compound, and it is more preferred to use it in the 80-100-mol% of range. There is a possibility that the crystallinity of the zinc oxide in the particles which will be obtained if less than said range may become low.

[0029]As for a monocarboxylic acid compound, 50 to 200 times are preferred to Md of Md compound at a mole ratio. Eight or less times 1.90 or more-time are preferred at the mole ratio to Zn. It is because the particles which are excellent in monodisperse nature and are excellent in antistatic property when a film is formed, and the grant performance of IR cut performance are easy to be obtained. As alcohol used with the manufacturing method of zinc oxide system particles, aliphatic series monohydric alcohol (methanol, ethanol, and isopropyl alcohol.) n-butanol, t-butyl alcohol, stearyl alcohol, etc., aliphatic series unsaturation monohydric alcohol (allyl alcohol and clo chill alcohol.) alicyclic monohydric alcohol (cyclopentanol.), such as propargyl alcohol aromatic monohydric alcohol (benzyl alcohol.), such as cyclohexanol monohydric alcohol; alkylene glycol [, such as heterocyclic monohydric alcohol,] (furfuryl alcohol etc.) (ethylene glycol.), such as cinnamyl alcohol and methylphenylcarbinol Propylene glycol, a trimethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1, 8-octanediol, 1,10-Decanediol, a pinacol, a diethylene glycol, triethylene glycol, etc., the aliphatic series glycols which have an aromatic ring, and alicyclic glycols (hydrobenzoin, a benzpinacol, phthalyl alcohol, etc.) (cyclopentane 1,2-diol and cyclohexane-1,2-diol.) polyoxy alkylene glycol (a polyethylene glycol.), such as cyclohexane-1,4-diol a polypropylene glycol etc. -- etc. -- glycols; -- propylene glycol monoethyl ether. Propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, Tripropylene glycol monomethyl ether, 3-methyl-3-methoxybutanol, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Derivatives, such as monoether of the above-mentioned glycols, such as triethylene glycol monomethyl ether and ethylene glycol mono- acetate, and monoester; Hydroquinone, Aromaticdiol, these monoether, and monoester, such as resorcinol and 2,2-bis(4-hydroxyphenyl)propane; it is trihydric alcohol and these monoether, monoester, a diether, diester, etc., such as glycerin. these alcohol -- one sort -- or two or more sorts are used.

[0030]As for alcohol, it is preferred to consider it as 1-30 times the amount to the zinc oxide equivalent weight of brewing Mino Zn compounds, and it is more preferred to consider it as 15-25 times the amount. As for the mole ratio of alcohol to a monocarboxylic acid compound, it is preferred to consider it as one to 10 times. The zinc oxide system particles which contain the above Ma(s) in a solution (S) by making the compound of Ma contain in the less than one range by the atomic ratio (Ma/Md) of Ma of Ma compound to Md of Md compound contained in a solution (S) can be

obtained easily. By making Ma live together, it is effective in the particles which are excellent in monodisperse nature being obtained irrespective of the amount of metal Md (addition ratio to zinc). The zinc oxide system particles made into the purpose under the conditions which could lessen quantity of the solvent required in order to obtain the solution (S) containing Md compound and Zn compounds on the process, therefore were excellent in the economic target are obtained.

[0031] From a point of the monodisperse nature of the particles obtained, coexistence of Ma changes also with kinds of metal Md, when the amount of metal Md to Zn is high, but. It is effective when Md/Zn (atomic ratio) is not less than 3%, Md is IIIB fellows and IVB fellows, Md is except the above, and Md/Zn (atomic ratio) is 1% or more. as the desirable method of preparation of a solution (S) -- ** -- beforehand Md compound with the solution (Sa) obtained by carrying out the uniform dissolution in the solvent. The liquid (a solution or suspension may be sufficient) containing a zinc compound or a zinc compound is mixed, method ** which obtains the solution (S) containing Md and zinc -- beforehand some of Md compounds and zinc compounds with the solution (Sb) obtained by carrying out the uniform dissolution in the solvent. The liquid (a solution or suspension may be sufficient) containing the remaining zinc compound or zinc compound is mixed, and the method of obtaining the solution (S) containing Md and zinc is mentioned. What is necessary is just to add Ma compound, when preparing Sa from the above-mentioned Reason if needed in **, and preparing Sb in **. In order to obtain the above-mentioned solution (Sa, Sb), it is preferred to heat at the temperature which can usually be heated above 50 ** and carries out reflux. As a suitable solvent used by Sa and Sb, one sort or two sorts or more of mixtures, such as monocarboxylic acid mentioned above, an anhydride of this monocarboxylic acid, water, and alcohol mentioned above, are mentioned.

[0032] The dispersion liquid of the particles where crystallite size gathered and which do not have condensation are easy to be obtained by heating a solution (S) at 150-200 ** preferably, and depositing zinc oxide system particles. Further in the bottom of the non-oxidizing atmosphere of 0.1% or less of an oxygen density the atmosphere of a gas portion the obtained dispersion liquid in a well-closed container, By performing heat-treatment of less than 24 hours 1 minute or more at not less than 200 ** the temperature below 400 **, crystallinity is higher and the particles excellent in grant of infrared interception nature when a film is formed, and antistatic property are obtained. By making temperature of heat-treatment into the range of 220-300 **, the particles excellent in especially monodisperse nature can be obtained. Since infrared cutoff performance and antistatic property may fall if it carries out the bottom of an oxidizing atmosphere, it is not desirable.

[0033] An atomic number [as opposed to zinc for the total content of the impurity H in a solution (S)]. (However, in the case of a sulfuric acid root, in the case of the atomic number of S, and a nitric acid root, it calculates as an atomic number of N) By a ratio, by considering it as 0.001% or less 0.01 more% or less 0.1% or less especially more preferably 0.5% or less, Zinc oxide system particles with few above impurities H can be obtained easily. It contains, also when the impurity H is not included at all in a solution (S), of course.

[0034] When a solution (S) contains carbonate in 0.001 to 5% of range by the number ratio of mols of CO_3 to Zn of Zn compounds contained in a solution (S), controlled photocatalyst activity particles can also be obtained. By the above process, $0.5 < \text{Ds}(002)/\text{Ds}(100) < 1.0$, $5 \leq \text{Dw} \leq 30$ (nm), and $0 \leq \text{Aw} \leq 0.5$ (%) can be satisfied, and the impurity H can obtain 0.1% or less of particles preferably 0.5% or less by an atomic ratio to zinc. [A binder component] A binder component used by

this invention is an ingredient in which a coat which has film formation performance, combines zinc oxide system particles, is excellent in antistatic property, and is excellent in optical properties, such as transparency and colorlessness, endurance, adhesion, and flexibility is made to form. This binder component may contain binder resin as an essential ingredient, and may contain a cross linking agent if needed.

[0035]As binder resin, various synthetic resins (thermosetting, ultraviolet curing nature, electron beam hardenability, moisture curing nature, these concomitant use, etc.), a natural resin, etc. of thermoplasticity or hardenability can be mentioned. As a synthetic resin, for example Alkyd resin, amino resin, polyvinyl resin, An acrylic resin, an epoxy resin, polyamide resin, polyurethane resin, Thermosetting unsaturated polyester resin, phenol resin, chlorinated polyolefin resin, silicone resin, acrylic silicone resin, a fluoro-resin, xylene resin, petroleum resin, ketone resin, rosin denaturation maleic acid resin, liquid polybutadiene, coumarone resin, etc. can be mentioned -- these -- one sort -- or two or more sorts are used. as a natural resin, shellac, rosin (turpentine), rosin ester, hardened rosin, decolorization shellac, white shellac, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0036]As alkyd resin, for example Super-short oil alkyd resin, short oil alkyd resin, Pure alkyd resin, such as middle oil alkyd resin, long oil alkyd resin, and super-long oil alkyd resin; by rosin, phenol, epoxy, styrene, urethane, silicon, amino resin, a natural resin, synthetic resin, a polymerization nature monomer, etc. modified-alkyd-resin; which denaturalized the above-mentioned pure alkyd resin -- oil free alkyd resin containing oil free alkyd resin and the amount of polymers oil free alkyd resin can be mentioned -- these -- one sort -- or two or more sorts are used.

[0037]As amino resin, for example Butylated melamine resin, methylation melamine resin, Melamine resin and melamine formaldehyde resin, such as benzoguanamine resin; Butyl-ized urea resin, urea resin and urea resin; -- the amino alkyd copolycondensation resin etc. which carried out copolycondensation of melamine resin, or urea resin and alkyd resin can be mentioned -- these -- one sort -- or two or more sorts are used. [, such as butyl-ized urea melamine resin,]

[0038]the polymerization nature monomer (vinyl acetate.) of polyvinyl chloride, VCM/PVC, and others as polyvinyl resin Vinyl chloride resin, such as a copolymer with lower-fatty-acid vinyl ester, such as vinyl propionate, a vinylidene chloride, etc.; Polyvinyl acetate, vinyl acetate and other polymerization nature monomers (ethylene, propylene, and styrene.) Vinyl acetate resin, such as a copolymer with acrylic ester, vinyl propionate, a vinylidene chloride, etc.; Polyvinyl alcohol of the saponification degree of several kinds, various denaturation (silicone modification, carboxyl denaturation, and amino modifying -- it and) [epoxy-] Polyvinyl alcohol resin, such as polyvinyl alcohol, such as mercapto denaturation; A polyvinyl butyral, butyral resin (vinyl alcohol, vinyl acetate, etc.) of vinylbutyral and other polymerization nature monomers, such as a copolymer, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0039]The copolymer which uses acrylic acid (meta) and its ester as the main ingredients of a main chain as the above-mentioned acrylic resin, for example; (meta) The copolymer of acrylic ester, Thermoplastic acrylic resins, such as a copolymer of acrylic ester and polymerization nature monomers, such as vinyl system monomers (styrene, vinyl ester, etc.); (Meta) To the monomer which constitutes a thermoplastic acrylic resin. (Meta) The hydroxy alkyl ester of acrylic acid and acrylic acid (meta), (Meta) Thermosetting acrylics, such as what added a cross linking agent component or heat cure ingredients, such as glycidyl ester of acrylic acid; (meta) Styrene other

than an acrylic system monomer, The moisture curing which makes a copolymer component the copolymer which denaturalized by monomers, such as vinyltoluene and vinyl acetate, and the acrylic monomer which has a silyl group (alkoxy silyl groups) of hydrolysis nature is possible, Epoxy curing type acrylic resin in which the silicon concentration contained in resin makes a copolymer component the acrylic monomer which has silyl modified resin; basicity nitrogen which is 1 or less weight %, and uses an epoxy compound for a cross linking agent component; The acrylic resin etc. which have an oxidative polymerization function can be mentioned, these -- one sort -- or two or more sorts are used.

[0040]As an epoxy resin, for example A bisphenol A type, a bisphenol female mold, A 2,6-xyleneol type, a bromination bisphenol A type, a phenol novolac type, glycidyl ether type [, such as an orthocresolnovolak type,]; -- glycidyl ester type [of synthetic fatty acid, such as dimer acid,]; -- an aromatic amine type (glycidyl amine type) etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0041]A hardening agent may be used together when using an epoxy resin as binder resin. As a hardening agent, for example Polysulfone, aliphatic polyamine, aromatic polyamine, polyamide, tertiary amine, diethylamino propylamine, imidazole, a tertiary amine salt, alicyclic amine, an acid anhydride, boron fluoride and amine salt, dicyandiamide, polyphenol, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0042]As polyurethane resin, for example An oil denaturation type, a moisture curing type, a heat cure type, 1 liquid type polyurethane resin [, such as a lacquer type,]; -- a polyol hardening type (acrylic polyol.) various polyols, such as polyester polyol and polyether polyol, and an isocyanate prepolymer should put together -- two-component type polyurethane resin, such as a catalyst hardening type, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0043]As phenol resin, for example Resol type phenol resin and novolac type phenol resin, what denaturalized these phenol resin with an epoxy resin, alkyd resin, polyvinyl butyral resin, polyamide, an acrylic resin, drying oil, rosin, petroleum resin, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0044]as chlorinated polyolefins, chlorinated polyethylene resin, chlorinated polypropylene resin, chlorinated rubber, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As silicone resin (organopolysiloxane), the straight-silicone-resin; alkyd denaturation of for example, dimethyl silicone, methylphenyl silicone, etc., epoxy denaturation, polyester denaturation, acrylic modification, the denaturation silicone resin by which urethane denaturation was carried out, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0045]as for acrylic silicone resin, the silicon concentration contained in resin is 1 weight % or more of a thing, for example, silicon concentration can mention 1 weight % or more of an alkoxy-silyl-groups content acrylic copolymer etc. -- these -- one sort -- or two or more sorts are used. As a fluoro-resin, for example Polyvinyl fluoride, polyvinylidene fluoride, A chlorotrifluoroethylene copolymer, a tetrafluoroethylene hexafluoropropylene copolymer, Thermoplastic fluoro-resins, such as an ethylene chlorotrifluoroethylene copolymer and a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer; Fluoro olefins, such as tetrafluoroethylene, alkyl vinyl ether, hydroxyalkyl vinyl ether, Solvent meltable type fluoro-resins, such as an alternating copolymer (FEVE resin) with vinyl ether, such as carboxy alkyl vinyl ether; A vinylidene fluoride hexafluoropropylene copolymer, A tetrafluoroethylene propylene copolymer, fluorine-containing silicone series fluorocarbon rubber, Fluorine-containing vinyl ether system fluorocarbon rubber, fluorine-containing phosphazene system

fluorocarbon rubber, fluorocarbon rubber [, such as a fluorine-containing thermoplastics elastomer]; -- other fluorocarbon rubbers, such as a fluorine-containing epoxy resin, fluorine-containing polyimide, and fluorine-containing silicone, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0046]Water and/or an organic solvent are distributed or a thermoplastic fluoro-resin is used with the form of a granular material, although there are some which are not dissolved in a solvent. The solvent meltable type fluoro-resin which introduced bridge construction ingredients, such as hydroxyl, can be hardened by an isocyanate or melamine resin. as xylene resin, denaturation xylene resin, such as native xylene resin; phenol denaturation and rosin denaturation, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0047]as petroleum resin, petroleum resin of petroleum resin; carbon number 5 system of carbon number 9 system, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As a synthetic resin, the rubber of nature, such as ethylene-propylene copolymerization rubber, polybutadiene rubber, a styrene butadiene rubber, and acrylonitrile butadiene copolymerization rubber, or composition, etc. may be used. As an ingredient used together with a synthetic resin, a cellulose nitrate, cellulose acetate butylate, cellulose acetate, ethyl cellulose, hydroxypropylmethylcellulose, hydroxyethyl cellulose, etc. can be mentioned.

[0048]About the form of the binder resin used for an antistatic coating constituent, there is no limitation in particular and a solvent meltable type, a water soluble type, an emulsion type, distributed type (arbitrary solvents, such as water/organic solvent), etc. can be mentioned. As binder resin of a water soluble type, water-soluble alkyd resin, water-soluble acrylic modification alkyd resin, water-soluble oil free alkyd resin (water-soluble-polyester resin), water soluble acrylic resin, water-soluble epoxy ester resin, water-soluble melamine resin, etc. can be mentioned, for example.

[0049]As emulsion type binder resin, for example An alkyl acrylate (meta) copolymerization dispersion; vinyl-acetate-resin emulsion, A vinyl acetate copolymerization resin emulsion, an ethylene-vinyl acetate copolymerization resin emulsion, An acrylic ester (**) polymerization resin emulsion, a styrene acrylic ester (**) polymerization resin emulsion, an epoxy resin emulsion, a urethane resin emulsion, an acrylic silicone emulsion, a fluoro-resin emulsion, etc. can be mentioned.

[0050]When using the antistatic coating constituent of this invention for manufacture of the below-mentioned antistatic film, etc., from a viewpoint of film formation conditions, such as forming temperature, the flexibility of the film obtained, or weatherability, polyurethane resin, an acrylic resin, a fluoro-resin, etc. are preferred as binder resin. As a cross linking agent used as a binder component, For example, the cross linking agent used for drying oil systems, such as air (oxygen); Polyester resin, such as an unsaturated monomer of monofunctional or many organic functions, The cross linking agent used for a poly acrylic resin and an epoxy resin; The 1st class, polyamine containing the 2nd class amino group, The cross linking agent used for the binder resin which has epoxy groups, such as polyamide, the amino resin which has a methylol group and the polybasic acid which has a carboxyl group, and high acid number polyester; The polyisocyanate which has an isocyanate group, The amino group of the polyisocyanate which has a urethane group, a methylol group, the 1st class, and/or the 2nd class, The cross linking agent used for the binder resin which has carboxyl groups, such as a cross linking agent; metal chelator used for the binder resin which has hydroxyl groups, such as amino resin which has an alkoxy methylene group; Moisture, the cross linking agent etc. which are used for the binder resin which

has silicone groups, such as a polyfunctional epoxy compound and hydroxyl group-containing compound, can be mentioned -- these -- one sort -- or two or more sorts are used.

[0051]As a polyisocyanate of the above-mentioned cross linking agents, For example, bird RENJISHISO cyanate, 4, and 4'-diphenylmethane diisocyanate, Hexamethylene di-isocyanate, naphthylene-1,5-diisocyanate, Diisocyanate, such as isophorone diisocyanate and dicyclohexyl methane-4,4'-diisocyanate; The adduct of tolylene diisocyanate and trimethylolpropane, The adduct of hexamethylene di-isocyanate and trimethylolpropane, The trimethylolpropane adduct of isophorone diisocyanate and the above-mentioned diisocyanate, such as an adduct of trimethylolpropane; Isocyanurate denaturation tolylene diisocyanate, Isocyanurate denaturation hexamethylene di-isocyanate, isocyanurate denaturation thing [of the above-mentioned diisocyanate, such as isocyanurate denaturation isophorone diisocyanate,]; -- biuret denaturation thing [of the above-mentioned diisocyanate, such as biuret denaturation hexamethylene di-isocyanate]; -- the above-mentioned diisocyanate and a trimethylolpropane adduct. An isocyanurate denaturation thing, a biuret denaturation thing, etc. Prepolymer-izing, the polymer-ized denaturation thing; above-mentioned diisocyanate, a trimethylolpropane adduct, The isocyanate group in an isocyanurate denaturation thing, a biuret denaturation thing, prepolymer-izing, and the polymer-ized denaturation thing Alcohols, the block-type polyisocyanate etc. which were protected with phenols, oxime, an active methylene compound, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[An antistatic coating constituent and a paint article] The antistatic coating constituent concerning this invention is a constituent which uses the above-mentioned zinc oxide system particles and a binder component as an essential ingredient.

[0052]Although there is no limitation in particular about the rate over the total solids of a binder component of zinc oxide system particles, and the zinc oxide system particle total quantity, it is 60 to 80 weight % still more preferably 50 to 95weight % preferably. At this time, hardening agents, such as a cross linking agent, shall also be included in a binder component. There is a possibility that transparency and antistatic property may fall that the rate of zinc oxide system particles is less than 50 weight % to said total-solids total quantity. On the other hand, when the rate of zinc oxide system particles exceeds 95 weight %, there is a possibility that optical properties, such as transparency and colorlessness, endurance, weatherability, adhesion, and flexibility may fall. Especially about weatherability, when the rate of zinc oxide system particles exceeds 80 weight %, it may fall rapidly. In order to solve this problem, it is preferred that silane coupling agent treatment, said M-X group content polymer processing, etc. carry out a surface modification to zinc oxide system particles beforehand, but the manufacturing cost of zinc oxide system particles may rise, and it may be necessary to improve a binder component.

[0053]Without reducing antistatic property as the antistatic coating constituent of this invention is what contains a conductive adjuvant further, the content of zinc oxide system particles can be reduced and, moreover, the weatherability of the coat obtained from an antistatic coating constituent, adhesion, flexibility, endurance, etc. can be raised. It is thought that antistatic property does not fall because a conductive adjuvant carries out the role of ***** which connects zinc oxide system particles and antistatic efficiency increases even if it reduces the content of zinc oxide system particles, when a conductive adjuvant is included.

[0054]As a conductive adjuvant used by this invention, what at least a part of the surface becomes from conductive substances, such as metal, conductive metallic

oxide, and a conductive organic matter, is preferred. The conductive coat adjuvant which should just have covered at least a part of below-mentioned core material with the conductive substance by the surface consisting of conductive substances at least may be sufficient as a conductive adjuvant. as metal used for a conductive adjuvant, alloys, such as metal simple substance; stainless steel, such as iron, nickel, copper, tin, aluminum, lead, zinc, and silver, copper and a zinc alloy, copper, a tin alloy, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0055]as conductive metallic oxide used for a conductive adjuvant, a zinc oxide, Sb dope tin oxide, aluminum dope zinc oxide, Sn dope indium oxide, stannic acid cadmium, rhenium oxide, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As a conductive organic matter used for a conductive adjuvant, For example, Polyacethylene (dopants, such as iodine.) What was doped. it contains --; polypyrrole (dopants, such as periodic acid ion.) What was doped. it contains --; polythiophene (dopants, such as periodic acid ion.) What was doped. it contains -- polythiophenes, such as; poly aniline (what doped dopants, such as EMERARUJIN base, is included); poly para-phenylene (what doped dopants, such as AsF₅, is included); polyphenylene vinylene; polyalkylthio Foehn,. heterocyclic content polymer [, such as polypyrrole,]; -- conductive polymers, such as a derivative produced by introducing an ester group, an alkyl group, etc. into aromatic ring content polymer, such as poly para-phenylene, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0056]As a core material which constitutes a conductive coat adjuvant, for example White mica, phlogopite, Nature, such as lepidolite, sericite, and fluoride phlogopite, or synthetic mica, sepiolite (argillite), Kaolinite, talc, bentonite, montmorillonite, a smectite, Organic fiber, such as nature, such as pyrophyllite, or synthetic argillite, nylon, polyester, potassium titanate, boric acid aluminum, titanium oxide, silicon carbide, ferric oxide, a zinc ferrite, a magnesium ferrite, glass, silica, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0057]As a conductive substance used for covering at least a part of core material, the conductive metallic oxide which uses Sn, In, Zn, Sb, and Cd as the metal main ingredients can be mentioned, and it is colorless, or there is little coloring. Although there is no limitation in particular about a conductive adjuvant and the form of a core material, a globular shape, an ellipse globular shape, the shape of a cube, rectangular parallelepiped shape, the shape of a pyramid, tabular, rod form, etc. can be mentioned. Since the probability of contacting zinc oxide system particles among these as they are form of anisotropy with a comparatively large aspect ratio and large surface area, such as tabular and rod form, increases, zinc oxide system particles are connected and antistatic efficiency increases, it is desirable.

[0058]As what is easy to come to hand and it is easy to distribute in the coating composition of this invention as a conductive adjuvant, For example, metal or alloy fibers, such as iron, nickel, copper, aluminum, lead, zinc, and stainless steel, The conductive adjuvant of metal systems, such as scale-like silver and grape-like nickel; The letter tin-oxide particles of a needlelike Sb dope, The conductive adjuvant of conductive-metallic-oxide systems, such as tetrapod-like zinc oxide particles; Sb dope tin-oxide covering potassium titanate whisker, Conductive coat adjuvants, such as Sb dope tin-oxide covering boric acid aluminum whisker, Sb dope tin-oxide covering titanium oxide whisker, Sb dope tin-oxide covering mica, and polypyrrole covering polyester fiber, etc. can be mentioned.

[0059]When the conductive adjuvants used by this invention are tabular particles, there is no limitation in particular about thickness t, but 0.008-0.5-micrometer 0.005-1

micrometer [0.008-0.1-micrometer] is 0.008-0.05 micrometer still more preferably preferably. There is a possibility that the mechanical strength of tabular particles may fall that thickness t is less than 0.005 micrometer, and endurance may fall. On the other hand, when thickness t exceeds 1 micrometer, there is a possibility that transparency may fall. Although there is no limitation in particular also about length [of tabular particles] L , 0.05-20-micrometer 0.02-50 micrometers are 0.1-5 micrometers most preferably still more preferably. There is a possibility that antistatic property may fall that length L is less than 0.02 micrometer. On the other hand, when length L exceeds 50 micrometers, there is a possibility that endurance, adhesion, and flexibility may fall. the aspect ratio (L/t) of tabular particles -- desirable -- 2-500 -- further -- desirable -- 4-100 -- it is 6-50 most preferably.

[0060]The form of a board (projected type from a top) may be arbitrary, and tabular [as used in the field of this invention] may be form including circular, an ellipse, a spindle shape, a triangle, a quadrangle, a rhombus, a hexagon, an octagon, an infinite form, etc., and may be the shape of a piece, a thin film integrated circuit, the shape of a scale, hexagon-head tabular, etc., for example. When the conductive adjuvant used by this invention is a rod-like particle, there is no limitation in particular about the thickness d (the maximum thickness which passes along the center of a rod-like particle), but. 0.008-0.5-micrometer 0.005-1 micrometer [0.008-0.1-micrometer] is 0.008-0.05 micrometer still more preferably preferably. There is a possibility that the mechanical strength of a rod-like particle may fall that the thickness d is less than 0.005 micrometer, and endurance may fall. On the other hand, when the thickness d exceeds 1 micrometer, there is a possibility that transparency may fall. Although there is no limitation in particular also about length [of a rod-like particle] L , 0.05-20-micrometer 0.02-50 micrometers are 0.1-5 micrometers most preferably still more preferably. There is a possibility that antistatic property may fall that length L is less than 0.02 micrometer. On the other hand, when length L exceeds 50 micrometers, there is a possibility that endurance, adhesion, and flexibility may fall. the aspect ratio (L/t) of a rod-like particle -- desirable -- 2-500 -- further -- desirable -- 4-100 -- it is 6-50 most preferably.

[0061]The rod form as used in the field of this invention is form including a needle, filar, fibrous, whisker shape, the shape of a strip of paper, the shape of a star, tubular, a line, the arborescence for which two or more these gathered, the shape of a grape, etc. Conductive adjuvants may be other form particles other than tabular particles and a rod-like particle. In addition, as form particles, the particles of polyhedron shape, such as a globular shape, the shape of *****, the shape of a spindle body, the shape of a tetrahedron, the shape of hexahedron, the shape of octahedron, and the shape of a dodecahedron, etc. can be mentioned, for example. In addition, 3 axis pitch diameter of form particles $[(L+b+t)/3]$ is 0.05-2 micrometers still more preferably preferably. [0.005-10-micrometer]

[0062]When the antistatic coating constituent of this invention contains a conductive adjuvant with zinc oxide system particles and a binder component, Although there is no limitation in particular about the rate (a 100x conductivity adjuvant / zinc oxide system particles) over the zinc oxide system particles of a conductive adjuvant, it is 0.5 to 3 weight % most preferably 0.3 to 5weight % still more preferably 0.1 to 20weight %. There is a possibility that antistatic property may fall that the rate over the zinc oxide system particles of a conductive adjuvant is less than 0.1 weight %. On the other hand, when the rate of a conductive adjuvant exceeds 20 weight %, there is a possibility that endurance, adhesion, and flexibility may fall.

[0063]When the antistatic coating constituent of this invention contains a conductive

adjuvant, about the rate over the solid content of a binder component of a conductive adjuvant, and the zinc oxide system particle total quantity. Although there is no limitation in particular, it is 0.25 to 1.5 weight % most preferably 0.25 to 5 weight % still more preferably 0.05 to 9.5 weight %. There is a possibility that antistatic property may fall that the rate over said total quantity of a conductive adjuvant is less than 0.05 weight %. On the other hand, when the rate over said total quantity of a conductive adjuvant exceeds 9.5 weight %, there is a possibility that transparency, endurance, adhesion, and flexibility may fall.

[0064] The antistatic coating constituent of this invention may contain a solvent, and is suitably chosen by the kind of binder component, etc. As a solvent, for example Alcohols, aliphatic series, and aromatic carboxylic acid ester. organic system solvent; water; straight-mineral-oil; vegetable oil, such as ketone, ether, ether ester species, aliphatic series and aromatic hydrocarbon, and halogenated hydrocarbon, a wax oil, silicone oil, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0065] The antistatic coating constituent of this invention in addition to zinc oxide system particles, a binder component, and a conductive adjuvant, According to a military requirement, Hardening agent [, such as a cross linking agent,]; Curing catalyst; of a hardening auxiliary agent etc. plasticizer; -- defoaming agent and leveling agent; -- thixotropic agent; -- flattening; -- surface-active agent; -- fire retardant; -- paints wetting agent and dispersing agent; -- lubricant; -- ultraviolet ray absorbent; - - light stabilizer; -- antioxidant; -- in addition to this (heat) -- stabilizer; -- antiseptic; - - antifungal agent; -- seaweed-proofing agent; -- corrosion prevention and rust-preventives; -- color; -- additive agents, such as paints, may be contained.

[0066] The hardening agent used for drying oil systems, such as air (oxygen), as the above-mentioned hardening agent, for example; Polyester resin, such as an unsaturated monomer of monofunctional or many organic functions, The hardening agent used for a poly acrylic resin and an epoxy resin; The 1st class, polyamine containing the 2nd class amino group, The hardening agent used for the resinous principle which has epoxy groups, such as polyamide, the amino resin which has a methylol group and the polybasic acid which has a carboxyl group, and high acid number polyester; The polyisocyanate which has an isocyanate group, The amino group of the polyisocyanate which has a urethane group, a methylol group, the 1st class, and/or the 2nd class, The hardening agent used for the resinous principle which has carboxyl groups, such as a hardening agent; metal chelator used for the resinous principle which has hydroxyl groups, such as amino resin which has an alkoxy methylene group; Moisture, the hardening agent etc. which are used for the resinous principle which has silicone groups, such as a polyfunctional epoxy compound and hydroxyl group-containing compound, can be mentioned -- these -- one sort -- or two or more sorts are used.

[0067] As a polyisocyanate of the hardening agents, For example, bird RENJISHISO cyanate, 4, and 4'-diphenylmethane diisocyanate, Hexamethylene di-isocyanate, naphthylene-1,5-diisocyanate, Diisocyanate, such as isophorone diisocyanate and dicyclohexyl methane-4,4'-diisocyanate; An adduct of tolylene diisocyanate and trimethylolpropane, An adduct of hexamethylene di-isocyanate and trimethylolpropane, A trimethylolpropane adduct of isophorone diisocyanate and the above-mentioned diisocyanate, such as an adduct of trimethylolpropane; Isocyanurate denaturation tolylene diisocyanate, Isocyanurate denaturation hexamethylene di-isocyanate, isocyanurate denaturation thing [of the above-mentioned diisocyanate, such as isocyanurate denaturation isophorone diisocyanate,]; -- biuret denaturation thing [of the above-mentioned diisocyanate, such as biuret denaturation

hexamethylene di-isocyanate]; -- the above-mentioned diisocyanate and a trimethylolpropane adduct. An isocyanurate denaturation thing, a biuret denaturation thing, etc. Prepolymer-izing, the polymer-ized denaturation thing; above-mentioned diisocyanate, a trimethylolpropane adduct, An isocyanate group in an isocyanurate denaturation thing, a biuret denaturation thing, prepolymer-izing, and a polymer-ized denaturation thing Alcohols, a block-type polyisocyanate etc. which were protected with phenols, oxime, an active methylene compound, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0068]As a curing catalyst, for example Zinc naphthenate, calcium naphthenate, The curing catalyst used for drying oil systems, such as metal driers, such as an octylic acid zirconium, and an organic dryer; A redox system initiator, Polyester resin, such as a sensitizer (ultraviolet rays, an electron beam, etc. are required), a poly acrylic resin, The curing catalyst used for an epoxy resin; Amines and metallic compounds (heat is required), The hardening agent used for the binder resin which has hydroxyl groups, such as organic acid (heat is required) and inorganic acid (heat may be necessary); The curing catalyst etc. which are used for the binder resin which has silicone groups, such as metallic compounds and amines (humidity and heat are required), can be mentioned, these -- one sort -- or two or more sorts are used.

[0069]As a plasticizer, for example Dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, phthalic acid benzyl butyl ester, diisodecyl phthalate, tricresyl phosphate, diphenyl phosphate KUREJIRU, triphenyl phosphate dibutyl sebacate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0070]As a defoaming agent and a leveling agent, for example An acrylic defoaming agent, an acrylic leveling agent, a vinyl system defoaming agent, a vinyl system leveling agent, a silicone series defoaming agent, a silicone series leveling agent, a mineral system defoaming agent, a thixotropic agent (a thickening agent, an antisetling agent, a dripping inhibitor), etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0071]About a form of a thixotropic agent, there is no limitation in particular and a thixotropic agent for solvent systems, a thixotropic agent for drainage systems, etc. can be mentioned. As a thixotropic agent for solvent systems, for example An organic bentonite system, Thixotropic agents for inorganic particle system solvent systems, such as a superfines silica system and a surface treatment calcium carbonate system; An AMAIDO wax system, a hydrogenation castor oil wax system, a benzyliene sorbitol system, and metallic soap (zinc stearate.) An oxidation polyethylene system, such as aluminum stearate, a polymerization vegetable oil system, thixotropic agents for organic system solvent systems, such as a sulfate ester system anionic surface active agent system, a polyether ester type surfactant system, and a polycarboxylic acid amine salt system, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0072]as the thixotropic agent for drainage systems -- thixotropic agents for inorganic particle system water, such as for example, a superfines silica system and a magnesium aluminium silicate system, --; xanthan gum. thixotropic agents for organic system water, such as a guar gum, a sodium-polyacrylate system, acrylic acid and an acrylic ester copolymer system, a polyvinyl alcohol system, a polyethylene oxide system, and a urethane denaturation polyether system, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0073]as a flatting, hydrous silicon dioxides, such as white carbon, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as a surface-active agent -- for example, the Nonion system (a polyethylene-glycol type.)

anionic systems (a sulfate ester type and a sulfonic acid type.), such as a polyhydric alcohol type a carboxylic type, a phosphoric ester type, etc. can mention the surface-active agents (an amine acid type, a betaine type, etc.) of cation systems (an amine salt type, quarternary ammonium salt, etc.) and a both sexes system, etc. -- these -- one sort -- or two or more sorts are used.

[0074]as fire retardant, an antimony trioxide, aluminium hydroxide, a chlorinated paraffin, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as a paints wetting agent and a dispersing agent, the paints wetting agent and dispersing agent for solvent systems, a paints wetting agent, a dispersing agent for drainage systems, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0075]As the paints wetting agent and a dispersing agent for solvent systems, for example The amount unsaturation polycarboxylic acid of polymers, Polyether polyester carboxylate, the amount polyester acid polyamine salt of polymers, Polycarboxylic acid salt, the AMAIDO amine salt of the amount polyester acid of polymers, long chain polyamino AMAI drine compounds acid, The salt of aliphatic series poly AMAIDO, long chain polyamino AMAIDO, and polymer polyester acid, The various amount compounds of polymers, such as a polymer polyether system compound; Phosphoric ester, cationic compounds, such as salts of anionic compound; fatty amines, such as phosphate, fatty alcohol sulfuric ester salt, sulfonated oil, and alkyl-sulfonic-acid salts, and quarternary ammonium salt, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0076]As the paints wetting agent and a dispersing agent for water, for example The salt of the amount polycarboxylic acid of polymers, The salt of styrene maleic acid copolymer, the formalin condensate of naphthalene sulfonic acid, the salt of long chain alkyl organic sulfonic acid, the salt of ligninsulfonic acid, the salt of polyphosphoric acid and poly silicic acid, a long chain alkylamine salt, a polyethylene glycol derivative, a sorbitan fatty acid ester, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0077]as lubricant, aliphatic hydrocarbon system lubricant, high-class aliphatic series system alcohol and higher-fatty-acid system lubricant, fatty acid AMAIDO system lubricant, metallic soap system lubricant, fatty-acid-ester system lubricant, compound lubricant, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. as an ultraviolet ray absorbent, ultraviolet ray absorbents, such as a benzophenone series, a benzotriazol system, an oxalic acid anilide system, a cyanoacrylate system, and a triazine series, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0078]As the above-mentioned light stabilizer, for example Bis(1,2,2,6,6-pentamethyl 4-piperidyl)sebacate, hindered amine light stabilisers, such as methyl 1,2,2,6,6-pentamethyl 4-piperidyl sebacate and bis(2, 2, 6, and 6-tetramethyl 1-octyloxy 4-piperidyl)Deccan dioate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0079]as the above-mentioned antioxidant -- a phenol system (a mono- phenol system.) sulfur-compounds systems (dilauryl thiodipropionate.), such as a bisphenol system and a polymer system dimyristyl thiodipropionate etc. can mention phosphorus-compounds systems (a triphenyl boss fin, diphenyl isodecyl phosphate, etc.) etc. -- these -- one sort -- or two or more sorts are used.

[0080]in addition -- (heat) as stabilizer, tin series stabilizer, lead system stabilizer, stearic acid system stabilizer, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As tin series stabilizer, for example A di-n-octyltin

bis(isooctylthio glycolic acid ester)salt, Di-n-octyltin maleate polymer, a di-n-octyl SUZUJI lauric acid salt, Di-n-octyl tin series stabilizer, such as a di-n-octyltin ester maleate salt; A di-n-butyl tinbisma lane acid ester salt, Malete series compounds, such as a di-n-butyl tin ester maleate salt, a di-n-butyl SUZUBISU octylthio glycol ester salt, Mercapto system compounds, such as di-n-butyl tin beta-mercaptopropionic acid salt polymer, di-n-butyl tin series stabilizer [, such as laurate system compounds, such as di-n-butyl tin dilaurate,]; -- dimethyl tin series stabilizer, such as a dimethyltin bis(isooctylmercapto acetate)salt, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0081]as lead system stabilizer, 3 basicity lead sulfate, 2 basicity lead stearate, 2 basicity phosphorous acid lead, lead stearate, etc. can be mentioned, for example -- these -- one sort -- or two or more sorts are used. As stearic acid system stabilizer, for example Barium stearate, calcium stearate, magnesium stearate, aluminum stearate, lithium stearate, 12-hydroxylithium stearate, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0082]In addition (heat) as stabilizer, may use stabilizer other than the above-mentioned tin series stabilizer, lead system stabilizer, and stearic acid system stabilizer, and as such stabilizer, For example, behenic acid lithium, myristic acid lithium, triphenyl phosphite, diphenyl isodecyl phosphite, tris nonylphenyl phosphite, barium zinc liquefied compound stabilizer, calcium zinc liquefied compound stabilizer, cadmium barium zinc liquefied compound stabilizer, etc. can be mentioned -- these -- one sort -- or two or more sorts are used.

[0083]As an antiseptic, an antifungal agent, and a seaweed-proofing agent, for example 1,2-benziso thiazoline 3-one, 5-chloro-2-methyl-4-iso thiazoline 3-one, a p-chloro-m-xylene, 2-hydroxy methylamino ethanol, etc. can be mentioned -- these -- one sort -- or two or more sorts are used. as corrosion prevention and rust preventives, ethylamines and propylamine can be mentioned, for example -- these -- one sort -- or two or more sorts are used.

[0084]Weatherability of the antistatic coating constituent of this invention improves that it is what contains light stabilizer further. About the curing method of an antistatic coating constituent, a heat cure method is economically preferred. Although there is no limitation in particular about the manufacturing method of the antistatic coating constituent of this invention, the metaphor can mix a binder component to the dispersing element containing zinc oxide system particles, and can mention the method of mixing a conductive adjuvant further, etc. to it suitably.

[0085]The paint article concerning this invention forms in a base material surface the coat obtained from the above-mentioned antistatic coating constituent. Since this paint article equips that surface with the coat obtained from an antistatic coating constituent, it has the outstanding antistatic property and the weatherability of a coat, adhesion, and flexibility are high. As a base material, base materials, such as inorganic substances, such as glass and earthenware, and organic matters, such as resin, can be mentioned, especially the coat produced by applying an antistatic coating constituent to the base material surface of an organic matter has high weatherability, and it excels in flexibility, for example. About the form of the above-mentioned inorganic substance or an organic matter, there is no limitation in particular and form, such as film state, a sheet shaped, tabular, and fibrous, can be mentioned. Also among these, it is useful for the below-mentioned film, fiber, etc.

[0086]There is no limitation in particular as construction material of the resin used as a base material. For example, LDPE, HDPE, amorphous polyethylene, OPP (extension polypropylene), Polypropylene, such as CPP (crystallization

polypropylene), Polyolefin systems, such as polyisobutylene; EVA. (Ethylene-vinyl acetate copolymer) system; -- polystyrene system; -- elasticity or rigid-polyvinyl-chloride; -- EVOH (ethylene vinyl alcohol copolymer) system ;P VA system (vinylon system) ;P VDC system (polyvinylidene chloride); -- polyethylene terephthalate and polyethylenenaphthalate. Polyester system [, such as polybutylene naphthalate,], polycarbonate system; -- polyurethane system; -- polyamide system; -- polyimide system; -- polyacrylonitrile system; -- Pori Sall John system; -- polyether sulphone system; -- polyphenylene sulfide system; -- polyarylate system; -- polyether imide system; -- aramid system;. (meta-) acrylic; -- polyether ether ketone system; -- a tetrafluoroethylene ethylene copolymer, a tetrafluoroethylene hexafluoropropylene copolymer, polytetrafluoroethylene, polytrifluoroethylene, polyvinylidene fluoride, and polyvinyl fluoride. A tetrafluoroethylene perfluoro-alkyl vinyl ether copolymer, Fluororesin, such as polyvinyl fluoride, a tetrafluoroethylene hexafluoropropylene perfluoro-alkyl vinyl ether copolymer, and polychlorotrifluoroethylene resin, etc. can be mentioned.

[0087]In using for the use as which the very advanced visible light transmittance state of an optical lens etc. and transparency are required, A PMMA and MMA-styrene random copolymer, polycarbonate, Copolymers, such as transparent polypropylene, MMA, alpha-methylstyrene, or cyclohexyl methacrylate, The MMA denaturation type of ABS plastics, polystyrene, polyarylate, Pori Sall John, Various resin, such as polyether sulphone, transparent-epoxy-resin, Polly 4-methylpentene- 1, fluorinated polyimide, amorphous-fluorocarbon-resin, transparent phenoxy resin, and amorphous nylon resin and a fluorene series, can be used as a base material.

[0088]It becomes more important future still to use biodegradable resin as a base material from a disposal treatment problem as what meets the demand to biodegradability. For example, in such a case, Polly 3-hydroxy butylate, It is preferred to use biodegradable plastics, such as a kitchen chitosan system, a polyamino acid system, a cellulose type, a polycaprolactone system, an alginic acid system, a polyvinyl alcohol system, an aliphatic polyester system, a sugars system, a polyurethane system, and a polyether system, etc. as a base material.

[0089]It may be the purpose of improving the adhesion etc. of what arranged UV absorption film on the above-mentioned base material beforehand, and the coat and base material which are obtained from an antistatic coating constituent as a base material, and the thing thing which allotted the primer layer etc. beforehand may be used. Fluororesin, polyester system resin, acrylic (meta) resin, and polycarbonate system resin are preferred at the point that weatherability is high among a plastic film and a sheet also about the inside of these resin used as a base material.

[0090]The paint article of this invention can be manufactured by making the above-mentioned base material surface apply and harden an antistatic coating constituent, for example. About the method of applying an antistatic coating constituent to a base material surface, there is no limitation in particular and a dipping method, the roll coater method, the flow coat method, screen printing, the bar coating-machine method, the spin coater method, brush painting, a spray method, etc. can be mentioned.

[0091]After applying an antistatic coating constituent, in order to raise physical properties, such as chemical resistance, such as a water resisting property, solvent resistance, acid-proof, and alkali-proof, and abrasion-proof nature, it is preferred to make it harden by methods, such as heat curing (room temperature curing is included), moisture curing, ultraviolet curing, and electron beam hardening. There is no limitation in particular about the dry membrane thickness of the coat obtained from

an antistatic coating constituent, and 0.2-5-micrometer 0.5-50 micrometers are 0.5-2 micrometers most preferably still more preferably.

[0092] Although there is no limitation in particular about the surface resistance ρ of the coat obtained from an antistatic coating constituent, below $10^9 \Omega/\square$ are [below $10^{10} \Omega/\square$] $10^6 - 10^9 \Omega/\square$ most preferably still more preferably.

Although there is no limitation in particular about H_{ayes} of the coat obtained from an antistatic coating constituent, it is 1% or less most preferably 2% or less still more preferably 5% or less. H_{ayes} is the value produced by measuring with a turbidity meter.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Working example] Although the embodiment of this invention is shown together with a comparative example below, in addition, this invention is not limited to the following embodiment. A "part" and a "weight section" are shown in the following embodiments. Evaluation in this example was performed with the following technique.

1. The addition metal content of the evaluation <particle presentation> powder sample of zinc oxide system particles, other metal contents, and impurity H content were calculated by X-ray fluorescence, atomic absorption analysis, plasma emission spectrometry, gravimetric analysis, ultimate analysis, etc.

The <crystalline> powder X diffraction estimated. The passage of the following [valuation basis / crystalline].

[0094]

O There is a diffraction peak of ZnO crystal.

x: There is no diffraction peak of a ZnO crystal.

It asked by performing powder X diffraction measurement of the <crystallite diameter $D_s(hkl)$, D_w , and lattice strain A_w > powder sample.

By the $D_s(hkl)$: Scherrer method (based on the Cauchy approximation of function).

The size of microcrystal and 1 g of lattice strain <carboxylic acid group content> powder samples for which it asked using the crystallite diameter D_w of a vertical direction and the A_w : Wilson method from each diffracting plane (hkl) obtained are mixed in the sodium hydroxide solution of 0.01N. After stirring for three days, it measured by conducting ion chromatograph analysis of the supernatant fluid obtained by centrifugation operation.

By carrying out vacuum drying of a part of <particle concentration of dispersing element> dispersing element until it can remove volatile constituents, such as a

solvent, thoroughly in 100 **, obtain the end of dried powder and a retained material when this is heated at 500 ** among the air for 1 hour is used as a metallic oxide, It asked for the weight fraction to the dispersing element for a metallic oxide, and this value was made into the particle concentration (metallic-oxide conversion concentration) in a dispersing element.

2. To the evaluation <surface resistance> paint film surface of the coat obtained from an antistatic coating constituent. The golden Kushigata electrode was vapor-deposited (thickness 30nm**5nm), after neglecting it for 12 hours under the temperature-and-humidity condition shown in a table, and protection-from-light conditions, the electrometer 617 type by KESURE was used and the surface resistance value under the conditions was measured (impressed electromotive force 0.1V). Measurement of surface resistance was performed by the measuring condition (1) and (2) shown in the table.

[0095]The surface resistance of the coat after an accelerated weathering test did the accelerated weathering test on JIS B 7753-93 for 200 hours using the sunshine carbon arc light type lightfastness and the weather meter of a description, and measured subsequent surface resistance. The surface resistance after a water resistant test was immersed in the boiling water of pure water for 10 hours, and measured subsequent surface resistance.

With the <light transparency and transparency> turbidity meter (Nippon Denshoku Industries Co., Ltd. make NDH-1001 DP), the total light transmittance T and Hayes H were measured.

The transparency after a <transparent endurance> accelerated weathering test did the accelerated weathering test on JIS B 7753-93 for 200 hours using the sunshine carbon arc light type lightfastness and the weather meter of a description, and measured it after that. Using the turbidity meter (the Nippon Denshoku Industries Co., Ltd. make, NDH-1001 DP), measurement of transparency was asked for difference $\Delta H(\%) = H - H_0$ of initial haze value H_0 and haze value H after an examination, and it judged by the following valuation basis to it. The passage of the following [valuation basis / of transparency].

[0096]

The particle system analyzer according [the dispersibility of the zinc oxide system particles in the evaluation <dispersibility> antistatic coating constituent of an H< 10% of H< 5% of of H< 1% of AA: $\Delta A:1\% \leq \Delta B:5\% \leq \Delta C:10\% \leq \Delta H3$. antistatic coating constituent, etc.] to a dynamic-light-scattering system (Nozaki& Co., Ltd. NICOMP.) Using Model370, it asked for the mean particle diameter of the weight reference, and this was made into the mean-dispersion particle diameter Dd. The passage of the following [valuation basis / of dispersibility]. However, in the system which adds a cross linking agent and a curing catalyst, dispersibility was measured, before adding these.

[0097]

A: $Dd \leq 30nm$ B : the appearance of the dispersing element after settling a $\leq 50nm$ C: $50 nm < Dd \leq 100nm$ D: $100 nm < Dd$ <dispersion-stability> antistatic coating constituent on the degree of bath temperature of 50 ** for 30 days in the state where it was immersed in the organ bath, 30 nm<Dd was evaluated. The passage of the following [valuation basis / of a dispersion stability].

[0098]

- A: The state which does not carry out layer separation and does not have sediment.
- B: Although there is sediment, carry out re dispersion by shake.
- C: Sediment, even if it shakes, don't carry out re dispersion but gel.

When manufacturing a <pot-life> antistatic coating constituent, after adding a cross linking agent, it stirred at 20 ** and membranes were formed for every hour. About the obtained coat, transparency and hardenability were investigated and the maximum T of the mixing time in which these physical properties do not get worse was measured, respectively. The passage of the following [valuation basis / of pot life]. [0099]

A: The cotton which made $T > 6\text{-hour}$ B: $6\text{-hour} \geq T > 3\text{-hour}$ C: $T \leq 3\text{-hour}$ <hardenability> methyl ethyl ketone impregnate was ground 100 times on the coat, and the rubbing test was done. The surface state of the coat after a test was observed. The passage of the following [valuation basis / of hardenability]. [0100]

O : with no change.

** : A crack is seen on the surface.

x: A coat dissolves.

About the <adhesion> coat, the squares friction test by a cellophane tape was done, and adhesion was investigated. The passage of the following [valuation basis / of adhesion].

[0101]

A: 100/100 (completely with no exfoliation)

Bending was performed 3 less than [less than / less than / B: / 80/100 or more / 100/100C: / 50/100 or more / 80/100D:] 50/100 <flexibility> 90 degrees, and the crack generated on the surface and the existence of exfoliation were observed with the microscope. The passage of the following [valuation basis / flexible].

[0102]O : with no change.

** : Although exfoliation is not carried out, a crack occurs.

x: Exfoliate.

- Without carrying out the surface modification of the zinc oxide system particles P1 of the physical properties shown in the embodiment 1(1)-table 1, toluene was distributed and the dispersing element D1 (50 weight % of particle concentration) was prepared. To this dispersing element D1, the binder B1 grade shown in Table 3 was mixed by the combination shown below, it stirred at 25 ** to it for 3 hours, and the antistatic coating constituent C1 was obtained to it. The physical properties of the antistatic coating constituent C1 are shown in Table 5.

[0103]

Dispersing element D1 (50 weight % of particle concentration) 40 weight section Binder B1 (35% of nonvolatile matter concentration) 14.3 weight section Leveling agent (polysiloxane system) 0.05 weight section The antistatic coating constituent C1 obtained by the toluene 35 weight-section above. After applying by Bar Goh Tarr on the surface of the PET film and carrying out hot air drying for 2 minutes at 80 **, it was recuperated for three days at 50 **, and the coat (1) of 0.5 micrometer of dry membrane thickness was obtained. The various physical properties of a coat (1) are evaluated and the result is shown in Table 7.

[0104]- The surface modification which shows the zinc oxide system particles P2-P5 of the physical properties shown in Embodiment 1 (2) - the 1(7)-table 1 in Table 2 was performed, the solvent shown in Table 2 was distributed, and the dispersing elements D2-D5 were prepared. To these dispersing elements D2-D5, mixed addition of binder B-2 shown in Table 3 - the B7 grade was carried out by the combination shown in Table 4, respectively, and the antistatic coating constituents C2-C7 were obtained like Embodiment 1 (1). The physical properties of the antistatic coating constituents C2-C7 are shown in Table 5.

[0105]

[Table 1]

酸化亜鉛系粒子	添加金属含有量 (Zn基準)		粉末X線解析結果			結晶性	不純物H含有量 (Zn基準) モル%	他金属含有量 (Zn基準)		カルボン酸基含有量 重量%
	Md	モル%	Dw nm	Ds比 002/100	Aw %			金属	モル%	
P1	Al	1	20	0.79	0.10	○	<0.001	0		3.1
P2	In	4	12	0.60	0.01	○	<0.001	Na	0.1	0.5
P3	Ga	2.5	15	0.89	0.10	○	<0.001	Li	0.3	0.9
P4	Y	0.5	30	0.90	0.22	○	<0.001	Mg	0.2	4.3
P5	Hf	0.9	18	0.93	0.22	○	<0.001	0		2.4
P6	Ga	2.0	22	1.29	0.28	○	Cl:1.09	0		<0.001

[0106]

[Table 2]

酸化亜鉛系粒子	表面修飾剤	処理量 (酸化亜鉛系粒子基準) 重量%	分散体	分散体組成 粒子濃度 酸化物換算*1 重量%	溶媒
P 1	なし	—	D 1	5 0	トルエン
P 2	重合体 A * ²	1 0 . 0	D 2	4 0	トルエン
P 3	カルボキシル変性ポリメチルシロキサン	1 . 0	D 3	4 0	酢酸ブチル
P 4	アルキルセートアルミニウムソノプロレート	2 . 4	D 4	2 0	酢酸ブチル
P 5	ヒドロキシカルトリメチシラン	1 8	D 5	3 0	イソブチル
P 6	なし	—	D 6	1 0	トルエン

*1: 600℃焼成時の灰分重量から求めた。

*2: 重合体Aは、メチルメタクリレート(20部)、シロキシルメタクリレート(75部)およびメチルシロキシルトリメチシラン(5部)を重合して得られた重合体

[0107]

[Table 3]

バインダー種類		備 考			
		酸価	数平均 分子量	OHV	
B 1	アクリル樹脂	0.5	30,000	-	HALSハイブリッドタイプ
B 2	アクリル樹脂	2	6,000	40	HALSハイブリッドタイプ
B 3	フッ素樹脂	2.5	10,000	24	
B 4	ポリウレタン樹脂 (ポリエステルポリオール)	8	3,000	250	
B 5	水溶性アクリル樹脂	pH 8	-	-	アミン 中和タイプ
B 6	アクリルシリコーン樹脂	-	12,000	-	Si-OCH ₃ 基含有
B 7	紫外線硬化型 ウレタンアクリレート	0.1	-	-	

[0108]

[Table 4]

実施例1	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	主溶媒	他の添加剤
(1)	C1	D1	B1	なし	28	78	トルエン	レベリング剤
(2)	C2	D2	B2	架橋剤A*3	45	73	トルエン	レベリング剤
(3)	C3	D2	B3	架橋剤A*3	35	80	トルエン	レベリング剤
(4)	C4	D4	B4	架橋剤A*3	50	80	酢酸ブチル	—
(5)	C5	D5	B5	なし	50	77	イソブチルアルコール	—
(6)	C6	D5	B6	なし	30	70	イソブチルアルコール	アクリル系塗料
(7)	C7	D3	B7	なし	60	82	酢酸ブチル	—

*1：600℃焼成時の灰分重量から求めた酸化物換算濃度。

*2：固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

*3：架橋剤Aは、イソシアレート変性アクリル系イソシアレートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアレート基がモル比で、1：1となるように添加した。

[0109]

[Table 5]

	帯電防止塗料組成物	塗膜	帯電防止塗料組成物物性			塗膜物性		
			分散性	分散安定性	ポットライフ	硬化性	密着性	可撓性
実施例1 (1)	C1	(1)	A	A	A	×	B	○
実施例1 (2)	C2	(2)	A	A	A	○	A	○
実施例1 (3)	C3	(3)	A	A	B	○	A	○
実施例1 (4)	C4	(4)	B	B	B	○	A	—
実施例1 (5)	C5	(5)	B	B	A	△	B	—
実施例1 (6)	C6	(6)	A	B	B	○	B	—
実施例1 (7)	C7	(7)	A	B	A	○	A	○
比較例1	C11	(11)	D	B	A	○	D	△

[0110]The antistatic coating constituents C2-C7 were formed on the conditions shown in Table 6, respectively, and the coat (2) - the coat (7) were obtained. The film formation condition which obtains a coat (1) from the antistatic coating constituent C1 was also shown in Table 6. The acquired physical properties of a coat (2) - a coat (7) are evaluated, and the result is shown in Table 7.

[0111]

[Table 6]

実施例 1	塗 膜	帯電防止塗料組成物	基 材	乾燥条件	膜 厚 ドライ μm
(1)	(1)	C1	PET74μm	80℃、2分間	0.5
(2)	(2)	C2	PET74μm	100℃、2分間	1
(3)	(3)	C3	フッ素74μm	100℃、2分間	3
(4)	(4)	C4	PMMA板	60℃、1時間	6
(5)	(5)	C5	ガラス	80℃、5分間	3
(6)	(6)	C6	PC板	常温、1カ月	5
(7)	(7)	C7	PET74μm	*1	1

*1：高圧水銀灯（80W/cm）、距離15cmで、5秒間

[0112]

[Table 7]

実施例1	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性 T H (%) (%)		透明耐 久性 促進耐 候性試 験後
		環境条件 (1)	環境条件 (2)	環境条件 (1)				
				促進耐候 性試験後	耐水試験 後			
(1)	(1)	4.4X10 ⁷	3.9X10 ⁷	8.0X10 ⁷	7.1X10 ⁷	86	3.3	A
(2)	(2)	8.7X10 ⁷	8.0X10 ⁷	9.0X10 ⁷	8.8X10 ⁷	87	2.5	AA
(3)	(3)	1.9X10 ⁸	2.0X10 ⁸	1.9X10 ⁸	1.8X10 ⁸	92	3.0	AA
(4)	(4)	3.2X10 ⁸	3.2X10 ⁸	3.5X10 ⁸	3.3X10 ⁸	89	1.0	A
(5)	(5)	7.1X10 ⁸	6.8X10 ⁸	>10 ¹⁰	>10 ¹⁰	88	0.8	C剥離
(6)	(6)	1.0X10 ⁸	9.9X10 ⁷	4.0X10 ⁸	3.2X10 ⁸	87	2.4	B
(7)	(7)	3.5X10 ⁸	3.1X10 ⁸	3.6X10 ⁸	3.6X10 ⁸	87	2.7	A

環境条件 (1) : 10℃、相対湿度20%

環境条件 (2) : 30℃、相対湿度60%

[0113]- In the dispersing element D1 (50 weight % of particle concentration) and binder B1 grade which were used in embodiment 2(1)-embodiment 1 (1). The whisker

shape particle powder (the thing in which the antimony content tin-oxide film was formed on the titania whisker surface, length:2micrometer, a diameter: 0.1-micrometer and aspect ratio:20) as a conductive adjuvant was added, and the antistatic coating constituent C8 of the presentation shown in Table 8 was prepared. The coat (8) was obtained by the film formation condition which shows the antistatic coating constituent C8 in Table 9. The physical properties of the obtained coat (8) are evaluated and the result is shown in Table 10.

[0114]- To the dispersing element D2, binder B-2, etc. which were used in embodiment 2(2)-embodiment 1 (2). The whisker shape particle powder (the thing in which the antimony content tin-oxide film was formed on the boric-acid aluminum whisker surface, length:18micrometer, a diameter: 0.8-micrometer and aspect ratio:20) as a conductive adjuvant was added, and the antistatic coating constituent C9 of the presentation shown in Table 8 was prepared. The coat (9) was obtained by the film formation condition which shows the antistatic coating constituent C9 in Table 9. The physical properties of the obtained coat (9) are evaluated and the result is shown in Table 10.

[0115]- In the dispersing element D2 and binder B3 grade which were used in embodiment 2(3)-embodiment 1 (2). The whisker shape particle powder (an antimony dope tin-oxide whisker, length:2.0micrometer, a diameter: 0.01-micrometer and aspect ratio:200) as a conductive adjuvant was added, and the antistatic coating constituent C10 of the presentation shown in Table 8 was prepared. The coat (10) was obtained by the film formation condition which shows the antistatic coating constituent C10 in Table 9. The physical properties of the obtained coat (10) are evaluated and the result is shown in Table 10.

[0116]- The antistatic coating constituent C11 was prepared like Embodiment 1 (1) except using the particles P6 of the physical properties shown in Table 1 instead of the zinc oxide system particles P1 used in comparative example 1-embodiment 1 (1). The physical properties of the antistatic coating constituent C11 are shown in Table 5. The antistatic coating constituent C11 was formed to the PET film like Embodiment 1 (1), and the coat (11) was obtained. The physical properties of the obtained coat (11) are evaluated and the result is shown in Table 10.

[0117]

[Table 8]

実施例2	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	導電性補助剤**/酸化亜鉛系粒子 重量%	主溶媒	他の添加剤
(1)	C8	D1	B1	なし	28	75	1	トルエン	レベリング剤
(2)	C9	D2	B2	架橋剤A**	25	65	2	トルエン	レベリング剤
(3)	C10	D2	B3	架橋剤A**	55	70	4	トルエン	レベリング剤

*1：600℃焼成時の灰分重量から求めた酸化物換算濃度。

*2：固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

*3：導電性補助剤として、実施例2（1）～2（3）に記載したウィスカー状粒子粉末を用いた。

*4：架橋剤Aは、イソシアレート変性ヘキサメチレンジイソシアネートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアネート基がモル比で、1：1となるように添加した。

[0118]

[Table 9]

実施例2	塗膜	帯電防止塗料組成物	基材	乾燥条件	膜厚 ドライ μm
(1)	(8)	C8	PETフィルム	80℃、2分間	0.5
(2)	(9)	C9	PETフィルム	100℃、2分間	1
(3)	(10)	C10	フッ素フィルム	100℃、2分間	3

[0119]

[Table 10]

	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性		透明耐 久性 促進耐 候性試 験後
		環境条件	環境条件	環境条件 (1)				
		(1)	(2)	促進耐候 性試験後	耐水試験 後	T (%)	H (%)	
実施例 2 (1)	(8)	8.8X10 ⁴	8.4X10 ⁶	9.0X10 ⁶	8.8X10 ⁶	85	3.8	A
実施例 2 (2)	(9)	2.2X10 ⁷	2.0X10 ⁷	3.0X10 ⁷	2.8X10 ⁶	84	4.2	AA
実施例 2 (3)	(10)	3.0X10 ⁶	2.8X10 ⁶	3.7X10 ⁶	3.9X10 ⁶	88	3.6	AA
比較例 1	(11)	1.2X10 ⁷	1.3X10 ⁷	—	—	82	22	C

環境条件 (1) : 10℃、相対湿度 20%

環境条件 (2) : 30℃、相対湿度 60%

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-172153

(43) 公開日 平成11年(1999) 6月29日

(51) Int.Cl.⁶

識別記号

F I

C 0 9 D 5/00
7/12

C 0 9 D 5/00
7/12

P
Z

審査請求 未請求 請求項の数 6 O L (全 22 頁)

(21) 出願番号 特願平9-343377

(22) 出願日 平成9年(1997)12月12日

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(54) 【発明の名称】 帯電防止塗料組成物およびその用途

(57) 【要約】

【課題】 湿度、温度等に対する依存性が低く、長期間安定した帯電防止性を有し、透明性、無色等の光学物性、耐久性、密着性および可撓性に優れる塗膜を形成し得る帯電防止塗料組成物およびその用途を提供する。

【解決手段】 帯電防止塗料組成物は、被膜形成性能を有するバインダー成分と、3価および／または4価をとる金属元素 (M d) と Z n とを金属成分とし X 線回折学的に酸化亜鉛結晶性を示す酸化亜鉛系粒子とを含む帯電防止塗料組成物において、前記酸化亜鉛系粒子が、F を除くハロゲン元素のイオンおよび／または原子、硫酸根 SO_4^{2-} および硝酸根 NO_3^- からなる不純物 H の合計含有量が、亜鉛に対する原子数 (ただし、硫酸根の場合は S の原子数、硝酸根の場合は N の原子数として計算する) 比で 0.5 % 以下である、ことを特徴とする。

【特許請求の範囲】

【請求項 1】被膜形成性能を有するバインダー成分と、3 価および／または 4 価をとる金属元素 (M_d) と Z_n とを金属成分とし X 線回折学的に酸化亜鉛結晶性を示す酸化亜鉛系粒子とを含む帯電防止塗料組成物において、前記酸化亜鉛系粒子が、F を除くハロゲン元素のイオンおよび／または原子、硫酸根 SO_4^{2-} および硝酸根 NO_3^- からなる不純物 H の合計含有量が、亜鉛に対する原子数 (ただし、硫酸根の場合は S の原子数、硝酸根の場合は N の原子数として計算する) 比で 0.5 % 以下である、ことを特徴とする帯電防止塗料組成物。

【請求項 2】前記酸化亜鉛系粒子が、結晶性酸化亜鉛に特有の回折ピークが現れ、2 つの格子面 (1 0 0) および (0 0 2) に対して、シェラー法 (コーシー関数近似) を用いて、垂直方向の結晶子の大きさ $D_s(h\ k\ l)$ を求めたとき、

$$D_s(0\ 0\ 2) / D_s(1\ 0\ 0) < 2$$

を満足し、

ウィルソン法を用いて求めた、結晶子の大きさを D_w とするとき、

$$1 \leq D_w \leq 100 \quad (\text{nm})$$

を満足する酸化亜鉛系粒子である、請求項 1 に記載の帯電防止塗料組成物。

【請求項 3】M_d が III B 族と IV B 族を除く金属元素である、請求項 1 または 2 に記載の帯電防止塗料組成物。

【請求項 4】前記酸化亜鉛系粒子の、前記バインダー成分の固形分および酸化亜鉛系粒子合計量に対する割合が、5.0 ~ 95 重量 % である、請求項 1 から 3 までのいずれかに記載の帯電防止塗料組成物。

【請求項 5】導電性補助剤をさらに含む、請求項 1 から 3 までのいずれかに記載の帯電防止塗料組成物。

【請求項 6】請求項 1 から 5 までのいずれかに記載の帯電防止塗料組成物から得られる塗膜を基材の表面に形成してなる塗装品。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、帯電防止塗料組成物およびその用途に関する。

【0002】

【従来の技術】従来、帯電防止塗料組成物としては、酸化亜鉛系や酸化錫系等の導電性金属酸化物微粒子；銅、ニッケル等の金属微粒子；アニオン系、カチオン系、両性の界面活性剤等を、帯電防止剤として含む塗料が知られている。これらのうち、金属酸化物、金属等の微粒子を含む組成物では、微粒子の粒子径が大きかったり、塗料および塗膜中での分散性が不十分であるために、透明性に優れ、着色のない帯電防止膜は得られなかった。また、帯電防止性を付与するために、塗料に微粒子を多く含ませる必要があり、得られる塗膜の可撓性や、密着性、耐候性等が十分でなく、塗膜を帯電防止フィルムと

して用いても満足できるものではなかった。

【0003】一方、界面活性剤を帯電防止剤として含む塗料では、透明性に優れる塗膜が得られるものの、界面活性剤に特有の伝導機構に基づいて、低湿度下での帯電防止性が不十分である等の環境依存性が高かった。また、帯電防止剤である界面活性剤の耐候性が低いため、塗膜の耐久性は十分ではなく、長期間使用すると、塗膜が劣化し、着色が生じたり、界面活性剤がブリードして、帯電防止性能が低下したり、ブロッキングが生じる等の実用上の種々の問題があった。

【0004】

【発明が解決しようとする課題】本発明が解決しようとする課題は、湿度、温度等に対する依存性が低く、長期間安定した帯電防止性を有し、透明性、無色等の光学物性、耐久性、密着性および可撓性に優れる塗膜を形成し得る帯電防止塗料組成物およびその用途を提供することである。

【0005】

【課題を解決するための手段】本発明にかかる帯電防止塗料組成物は、被膜形成性能を有するバインダー成分と、3 価および／または 4 価をとる金属元素 (M_d) と Z_n とを金属成分とし X 線回折学的に酸化亜鉛結晶性を示す酸化亜鉛系粒子とを含む帯電防止塗料組成物において、前記酸化亜鉛系粒子が、F を除くハロゲン元素のイオンおよび／または原子、硫酸根 SO_4^{2-} および硝酸根 NO_3^- からなる不純物 H の合計含有量が、亜鉛に対する原子数 (ただし、硫酸根の場合は S の原子数、硝酸根の場合は N の原子数として計算する) 比で 0.5 % 以下である、ことを特徴とする帯電防止塗料組成物。

【0006】前記酸化亜鉛系粒子が、結晶性酸化亜鉛に特有の回折ピークが現れ、2 つの格子面 (1 0 0) および (0 0 2) に対して、シェラー法 (コーシー関数近似) を用いて、垂直方向の結晶子の大きさ $D_s(h\ k\ l)$ を求めたとき、

$$D_s(0\ 0\ 2) / D_s(1\ 0\ 0) < 2$$

を満足し、ウィルソン法を用いて求めた、結晶子の大きさを D_w とするとき、

$$1 \leq D_w \leq 100 \quad (\text{nm})$$

を満足する酸化亜鉛系粒子であることが、好ましい。

【0007】この帯電防止塗料組成物は、導電性補助剤をさらに含むことが好ましい。本発明にかかる塗装品は、上記帯電防止塗料組成物から得られる塗膜を基材の表面に形成してなる塗装品である。

【0008】

【発明の実施の形態】以下では、まず、酸化亜鉛系粒子を説明した後、バインダー成分について説明し、最後に、本発明の帯電防止塗料組成物および塗装品について説明する。

〔酸化亜鉛系粒子〕本発明で用いられる酸化亜鉛系粒子は、酸化亜鉛系粒子本来の紫外線遮蔽性、可視光透過性

に加えて、赤外線非透過性、導電性等を示すとともに、湿度、温度等に対する依存性が低く、長期間安定した帯電防止性を示す。

【0009】酸化亜鉛系粒子は、3価および/または4価をとる金属元素(Md)とZnとを金属成分とする。Mdの含有量は、この金属成分の総原子数に対するMdの原子数の比で表して0.1~20%であることが好ましく、より好ましくは1~10%、さらに好ましくは3~8%である。前記範囲を上回ると組成、結晶サイズ等の均一性に富む微粒子となりにくく、前記範囲を下回ると熱線をはじめとする赤外線遮蔽性が不十分となり、帯電防止性が低下する。

【0010】添加元素であるMdとしては、B、Al、Ga、In、Tl、C、Si、Ge、Sn、Pb等のIIIB族元素およびIVB族元素の他、Sc、Y、Ti、Zr、Hf、V、Nb、Ta、Cr、Mo、W、Mn、Tc、Re、Fe、Ru、Os、Rh、Ir、La、Ce、Sb等が挙げられる。本発明で用いられる酸化亜鉛系粒子は、X線回折学的に酸化亜鉛結晶性を示すことが必要である。

【0011】酸化亜鉛系粒子の一次粒子の粒径としては、可視光波長域の光に対する透過性、赤外線遮断性に優れる点で、ウィルソン法(Wilson法)を用いて求めた結晶子径Dwが1~50nm(0.001~0.05μm)であることが好ましく、これらの1次粒子が2次凝集せずに分散していることが好ましい。酸化亜鉛系粒子の分散粒径Ddは、透明感が高く、組成物に添加したときに得られる組成物の色相に実質的に影響を与えない点、つまり透明性を高め、無色等の光学物性を付与する点から1μm以下であることが好ましい。より好ましくは0.5μm以下、さらに好ましくは0.1μm以下である。特に0.05μm以下が好ましい。透明性、密着性および耐候性等の点から単分散性が高いことが好ましい。単分散性は、結晶子径DwとDdとの比R(Dd/Dw)で定義され、Rが10以下であることが好ましく、3以下であることがより好ましく、特に1.5以下が好ましい。

【0012】分散粒径は、動的光散乱法、遠心沈降法などにより測定することができる重量基準の平均粒子径である。0.1μm未満の場合には、前者の測定方法を、0.1μm以上の場合には、後者の測定方法で測定される。本発明で用いられる酸化亜鉛系粒子としては、ポリマーがマトリックスを構成し、このマトリックス中に粒子が分散している形態のもの(ポリマー複合体粒子)も含まれ、中空状であると光拡散透過性に優れるものとなる。この粒子における酸化亜鉛系粒子の含有量は特に限定されないが、酸化亜鉛換算で複合体粒子全量に対して50~95重量%の範囲であることが望ましい。

【0013】複合化に用いられるポリマーとしては、アクリル樹脂系ポリマー、アルキド樹脂系ポリマー、アミ

ノ樹脂系ポリマー、ビニル樹脂系ポリマー、エポキシ樹脂系ポリマー、ポリアミド樹脂系ポリマー、ポリイミド樹脂系ポリマー、ポリウレタン樹脂系ポリマー、ポリエステル樹脂系ポリマー、フェノール樹脂系ポリマー、オルガノポリシロキサン系ポリマー、アクリルシリコン樹脂系ポリマー、ポリアルキレングリコール等の他、ポリエチレン、ポリプロピレン等のポリオレフィン系ポリマー、ポリスチレン系ポリマー、フッ素樹脂系などの熱可塑性または熱硬化性樹脂；エチレン-プロピレン共重合ゴム、ポリブタジエンゴム、アクリロニトリル-ブタジエンゴムなどの合成ゴムや天然ゴム；ポリシロキサン基含有ポリマー等を挙げることができる。

【0014】複合体粒子の形状としては、特に限定はないが、複合体粒子の表面は凹凸性に富むことが好ましい。表面に凹凸があると、複合体粒子を含む塗膜等においてバインダー成分等との親和性が高くなるためである。複合体粒子の平均粒子径としては、特に限定されないが、通常、0.001~10μmの範囲である。酸化亜鉛系粒子は、後述の被膜形成能を有するバインダー成分との相溶性、帯電防止塗料組成物中での分散性、分散安定性、酸化亜鉛との光触媒活性低減による耐候性付与等の目的で、表面修飾剤で処理されてなるものが好ましい。

【0015】好ましい表面修飾剤としては、前記したポリマーも使用できるが、耐候性付与の目的からは、M-X基を含有する化合物が挙げられる。ただし、Xは水素原子、ハロゲン原子およびOR¹から選ばれた少なくとも1種であり、R¹は水素原子、置換されていてもよいアルキル基、シクロアルキル基、アリール基、アラルキル基およびアシル基からなる群から選ばれた少なくとも1種であり、Mは金属元素、中でもSi、Ti、Zr、Alからなる群から選ばれる少なくとも1種が好ましい。分散性(塗料や溶媒への分散性、塗料の安定性等)の付与の観点からは、有機高分子鎖を有するポリマーが挙げられる。耐候性および分散性の両面で好ましいものは、M-X基を含有し、且つ有機高分子鎖を有するポリマーであり、例えばポリシロキサン基含有ポリマーやアクリルシリコン等が挙げられる。

【0016】酸化亜鉛系粒子は、1価または2価の金属元素MaをMdに対するMaの原子比で、0.00001≤Ma/Md<1の範囲で含むことが好ましい。0.00001≤Ma/Md≤0.4の範囲であることがより好ましい。また亜鉛に対する原子比で、0.0001~2%の範囲であることが好ましい。Maの存在効果は、ZnO結晶中にMdを均質に(よりモノメリックな状態で)含有させ、しかも結晶表面を安定化し、2次凝集や結晶成長を抑制する点にある。したがって、単分散性の高い微細な結晶となる。したがって、Md量を多くして透明性に優れながら帯電防止性や赤外線遮蔽性を向上させることも可能となる。特開平8-253317号公報

では、アルカリ金属およびアルカリ土類金属の存在は好ましくないと記載されているが（第5頁第7欄第40～47行）、上記範囲で積極的に含むことで上記のような効果を奏するものである。Ma量が少なすぎると効果が発現せず、Ma量が多すぎると、該粒子を含有する塗膜の耐候性が低下する場合がある。1価または2価の金属元素Maとは、アルカリ金属元素および／またはアルカリ土類金属元素であり、リチウム、ナトリウム、カリウム、ルビジウム、セシウム、バリウム、マグネシウム、カルシウム、ストロンチウム、バリウム等が挙げられる。

【0017】本発明で用いられる酸化亜鉛系粒子は、Fを除くハロゲン元素（すなわち、塩素Cl、臭素Br、ヨウ素I）のイオンおよび／または原子、硫酸根 SO_4^{2-} および硝酸根 NO_3^- （不純物H）の合計含有量が、亜鉛に対する原子数（ただし、硫酸根の場合はSの原子数、硝酸根の場合はNの原子数として計算する）比で0.5%以下であることが重要である。より好ましくは0.1%以下、さらに好ましくは0.01%以下、特に好ましくは0.001%以下である。これには、不純物Hを全く含まない場合も含む。不純物Hを含有しないか、含有する場合にでもこの範囲を越えない場合にのみ、単分散性に優れた粒子となり、透明性は勿論、密着性や耐候性に優れた塗膜を形成することができる。

【0018】本発明で用いられる酸化亜鉛系粒子が、結晶性酸化亜鉛に特有の回折ピークである、格子面（100）、（002）、（101）に回折ピークを示し、以下の結晶子パラメータを満たすものであると、好ましい。シェラー法（Scherrer法）、すなわち、コーシー関数近似（Cauchy関数近似）を用いて、各回折面（hkl）に対して垂直方向の結晶子の大きさ $D_s(hkl)$ を求めたとき、 $D_s(002)/D_s(100) < 2$ を満足する。より好ましくは $D_s(002)/D_s(100) < 1.2$ 、さらに好ましくは $0.5 < D_s(002)/D_s(100) < 1.0$ である。この範囲にある場合に、赤外線非透過性および帯電防止性に優れるためである。

【0019】そして、ウィルソン法を用いて求めた、結晶子の大きさをDwとすると、 $1 \leq Dw \leq 100$ （nm）を満足することが好ましく、より好ましくは $5 \leq Dw \leq 30$ （nm）の範囲である。Dwが小さすぎると赤外線吸収性、赤外線透過性および帯電防止性が低下し、大きすぎると可視光に対する透明性が低下する。Dwは赤外線非透過性および帯電防止性の点からは結晶子の方が好ましく、可視光透過性の点からは小さい方が好ましい。Dwが5～30nmの範囲が両性能のバランスがとれる点で好ましいのである。Dwが前記範囲にある場合に、透明性、赤外線遮断性、紫外線吸収性および帯電防止性に優れたものとなる。さらに、ウィルソン法を用いて求めた格子歪みをAwとすると、Awが0 ≤

$Aw \leq 1$ （%）を満足すると好ましい。より好ましくは $0 \leq Aw \leq 0.5$ （%）の範囲である。Awが前記範囲にあるときには、Mdがよりモノメリックに含有されているためと考えられるが、赤外線遮断性および帯電防止性が最も高くなる。

【0020】本発明で用いられる酸化亜鉛系粒子の形状、粒子径等のモルフォロジーは特に限定されない。形状の具体例としては、球状、楕円球状、立方体状、直方体状、ピラミッド状、針状、柱状、棒状、筒状、りん片状、（六角）板状等の薄片状などが例示されるが、結晶子形態が上述の範囲にあることが好ましい。

【0021】本発明で用いられる酸化亜鉛系粒子は、カルボン酸のカルボキシル残基（カルボン酸基）を、ZnOに対する重量比で0.01～10%含有することが好ましく、0.1～5%含有することがより好ましい。カルボン酸基が粒子表面に存在することで、2次凝集が抑えられ、塗料としたときに透明性が高くなる。一方、カルボン酸基が多すぎると、形成した膜の赤外線遮断性および帯電防止性が低下する。カルボン酸基量が前記範囲にあるときに単分散性と帯電防止性と赤外線遮断性能の両方に優れたものとなる。また、酸化亜鉛系粒子は炭酸基をZnOに対する重量比で10%以下、好ましくは3%以下の範囲で含有していてもよい。

【0022】本発明で用いられる酸化亜鉛系粒子は、溶媒中に分散してなる分散体として取り扱うことができる。この分散体とは、酸化亜鉛系粒子と溶媒とを必須成分として含むものである。酸化亜鉛系粒子は、分散体総量に対する金属酸化物換算で2～80重量%の割合で含有されていることが好ましい。特に20～60重量%が好ましい。

【0023】溶媒としては、水、アルコール類、ケトン類、脂肪族および芳香族のカルボン酸エステル類、エーテル類、エーテルエステル類、脂肪族および芳香族の炭化水素類、ハロゲン化炭化水素類のほか、鉱物油、植物油、ワックス油、シリコン油等を挙げることができ、これらの溶媒が1種または2種以上使用される。汎用性の点から好ましい溶媒は、常圧に於ける沸点が40℃～250℃である、アルコール類、脂肪族および芳香族炭化水素類、ハロゲン化炭化水素類、芳香族および脂肪族カルボン酸エステル類、ケトン類、（環状）エーテル類、エーテルエステル類、水から選ばれる1種または2種以上の混合溶媒である。さらに、メタノール、エタノール、n-プロパノール、イソプロピルアルコール、n-ブタノール、エチレングリコール、プロピレングリコール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノブチルエーテル、エチレングリコールメチルエーテルアセテート、エチレングリコールエチルエーテルアセテート、エチレングリ

コールブチルエーテルアセテート、プロピレングリコールモノメチルエーテル、プロピレングリコールモノエチルエーテル、ジプロピレングリコールモノメチルエーテル、トリプロピレングリコールモノメチルエーテル、プロピレングリコールメチルエーテルアセテート、プロピレングリコールエチルエーテルアセテート、3-メチル-3-メトキシブタノール、3-メチル-3-メトキシブチルアセテート、トルエン、キシレン、ベンゼン、シクロヘキサン、n-ヘキサン、酢酸エチル、酢酸プロピル、酢酸ブチル、酢酸イソブチル、メチルエチルケトン、メチルイソブチルケトン、シクロヘキサノン、テトラヒドロフラン、水、からなる群から選ばれる1種または2種以上の混合溶媒を少なくとも含有する分散体は、分散性のより高い塗料組成物を得やすいため、特に好ましい。

【0024】次に、本発明で用いられる酸化亜鉛系粒子の製造方法について説明する。本発明で用いられる酸化亜鉛系粒子の製造方法としては、例えば、Zn化合物とMdの化合物と必要に応じてMaの化合物を含有する溶液(S)を加熱することにより酸化亜鉛系粒子を析出させる方法が挙げられる。酸化亜鉛系粒子の製造方法で用いられるZn化合物としては、金属亜鉛(亜鉛末)、酸化亜鉛(亜鉛華等)、水酸化亜鉛、塩基性炭酸亜鉛、置換基があってもよいモノ-またはジ-カルボン酸塩(たとえば、酢酸亜鉛、オクチル酸亜鉛、ステアリン酸亜鉛、シュウ酸亜鉛、乳酸亜鉛、酒石酸亜鉛およびナフテン酸亜鉛)、亜鉛の(アルキル)アルコキシド類、β-ジケトン、ヒドロキシカルボン酸、ケトエステル、ケトアルコール、アミノアルコール、グリコール、キノリン等の亜鉛のキレート化合物等の有機亜鉛化合物からなる群のうちから選ばれた少なくとも1つが好ましい。これらのZn化合物を用いるときは脱塩工程が不要となり、脱塩工程が必要な塩化亜鉛、硝酸亜鉛または硫酸亜鉛を使用するときに比べて工程が少なくなる。これらのZn化合物を用いると、不純物Hの含有量が少ない又はない、単分散性に優れる粒子が得られる。中でも、金属亜鉛(亜鉛末)、酸化亜鉛(亜鉛華)、水酸化亜鉛、塩基性炭酸亜鉛および酢酸亜鉛は、安価で取扱いが容易な点で好ましい。酸化亜鉛、水酸化亜鉛および酢酸亜鉛は、加熱過程に於ける酸化亜鉛の結晶の生成反応を阻害するような不純物を実質的に含まず、しかも、結晶と粒子との大きさや形状を制御しやすいので、さらに好ましい。特に気相法(フランス法、アメリカ法)で作られる酸化亜鉛が好ましい。気相法の酸化亜鉛は安価に入手できるばかりかモノカルボン酸の種類を任意に選択できることに加えて、これらの原料を用いることにより形状または粒子径等の制御された微粒子が特に得られ易く、不純物Hを含んでいないとしても極めて少ないので、特に好ましい。

【0025】酸化亜鉛系粒子の製造方法で用いられる金

属(Md)化合物としては、たとえば、金属Mdの、金属単体、合金などの金属；酸化物；水酸化物；炭酸塩、硝酸塩、硫酸塩、塩化物、フッ化物等のハロゲン化物等の無機塩類；酢酸塩、プロピオン酸塩、酪酸塩、ラウリン酸塩等のカルボン酸塩；金属アルコキシド類；β-ジケトン、ヒドロキシカルボン酸、ケトエステル、ケトアルコール、アミノアルコール、グリコール、キノリン等との金属キレート化合物、などの金属(Md)を含有する全ての化合物が挙げられる。金属MdがIn、Tl等のように複数の原子価をとり得る金属元素の場合、粒子生成過程で最終的に3価または4価に変化し得る低原子価の金属を含有する化合物からなる群から選ばれる少なくとも1つの化合物(この化合物は、金属単体や合金などの金属をも含む概念である)が使用される。これらの中で、金属Mdの金属、酸化物、水酸化物、炭酸塩(酸性、塩基性炭酸塩を含む)、酢酸塩、アルコキシド化合物、β-ジケトン化合物のような不純物Hを含まない有機金属錯体が不純物Hが少ない、あるいはない点で好ましい。

【0026】酸化亜鉛系粒子の製造方法で用いられる金属(Ma)化合物としては、たとえば、金属Maの、金属単体、合金などの金属；酸化物；水酸化物；炭酸塩、硝酸塩、硫酸塩、塩化物、フッ化物等のハロゲン化物等の無機塩類；酢酸塩、プロピオン酸塩、酪酸塩、ラウリン酸塩等のカルボン酸塩；金属アルコキシド類；β-ジケトン、ヒドロキシカルボン酸、ケトエステル、ケトアルコール、アミノアルコール、グリコール、キノリン等との金属キレート化合物、などの金属(Ma)を含有する全ての化合物が挙げられる。これらの中で、金属Maの金属、酸化物、水酸化物、炭酸塩(酸性、塩基性炭酸塩を含む)、酢酸塩、アルコキシド化合物、β-ジケトン化合物のような不純物Hを含まない有機金属錯体が不純物Hが少ない、あるいはない点で好ましい。

【0027】溶液(S)は、モノカルボン酸化合物およびアルコールを含むことが好ましい。モノカルボン酸化合物とは、分子内にカルボキシル基を1個だけ有する化合物である。該化合物の具体例としては、ギ酸、酢酸、プロピオン酸、イソ酪酸、カプロン酸、カプリル酸、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸等の飽和脂肪酸(飽和モノカルボン酸)；アクリル酸、メタクリル酸、クロトン酸、オレイン酸、リノレン酸等の不飽和脂肪酸(不飽和モノカルボン酸)；シクロヘキサンカルボン酸等の環式飽和モノカルボン酸類；安息香酸、フェニル酢酸、トルイル酸等の芳香族モノカルボン酸；無水酢酸等の上記モノカルボン酸の無水物；トリフルオロ酢酸、モノクロル酢酸、o-クロロ安息香酸等のハロゲン含有モノカルボン酸；乳酸などである。これらのモノカルボン酸化合物は単独で使用してもよいし、2

【0028】好ましいモノカルボン酸化合物は、1気圧

で200℃以下の沸点を有する飽和脂肪酸である。具体的には、蟻酸、酢酸、プロピオン酸、酪酸、イソ酪酸が単分散性に優れる粒子が得られやすい点で好ましい。該飽和脂肪酸は、モノカルボン酸化合物の総量に対して、60～100モル%の範囲で使用することが好ましく、80～100モル%の範囲で使用することがより好ましい。前記範囲を下回ると得られる粒子における酸化亜鉛の結晶性が低くなるおそれがある。

【0029】モノカルボン酸化合物は、Md化合物のMdに対してモル比で50～200倍が好ましい。また、Znに対するモル比で1.90倍以上8倍以下が好ましい。単分散性に優れ、膜を形成したときの帯電防止性およびIRカット性能の付与性能に優れる粒子が得られやすいためである。酸化亜鉛系粒子の製造方法で用いられるアルコールとしては、脂肪族1価アルコール（メタノール、エタノール、イソプロピルアルコール、n-ブタノール、t-ブチルアルコール、ステアシルアルコール等）、脂肪族不飽和1価アルコール（アリルアルコール、クロチルアルコール、プロパギルアルコール等）、脂環式1価アルコール（シクロペンタノール、シクロヘキサノール等）、芳香族1価アルコール（ベンジルアルコール、シンナミルアルコール、メチルフェニルカルビノール等）、複素環式1価アルコール（フルフリルアルコール等）等の1価アルコール類；アルキレングリコール（エチレングリコール、プロピレングリコール、トリメチレングリコール、1,4-ブタンジオール、1,5-ペンタンジオール、1,6-ヘキサンジオール、1,8-オクタンジオール、1,10-デカンジオール、ピナコール、ジエチレングリコール、トリエチレングリコール等）、芳香環を有する脂肪族グリコール類（ヒドロベンゾイン、ベンズピナコール、フタリルアルコール等）、脂環式グリコール類（シクロペンタン-1,2-ジオール、シクロヘキサン-1,2-ジオール、シクロヘキサン-1,4-ジオール等）、ポリオキシアルキレングリコール（ポリエチレングリコール、ポリプロピレングリコール等）等のグリコール類；プロピレングリコールモノエチルエーテル、プロピレングリコールモノエチルエーテル、ジプロピレングリコールモノメチルエーテル、トリプロピレングリコールモノメチルエーテル、3-メチル-3-メトキシブタノール、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、トリエチレングリコールモノメチルエーテル、エチレングリコールモノアセテート等の上記グリコール類のモノエーテルおよびモノエステル等の誘導体；ヒドロキノン、レゾルシン、2,2-ビス（4-ヒドロキシフェニル）プロパン等の芳香族ジオールおよびこれらのモノエーテルおよびモノエステル；グリセリン等の3価アルコールおよびこれらのモノエーテル、モノエステル、ジエーテルおよびジエステルなどである。これらのアルコールは、1種または2種以上使用される。

【0030】アルコールは、仕込みのZn化合物の酸化亜鉛換算重量に対して1～30倍量とすることが好ましく、15～25倍量とすることがより好ましい。また、モノカルボン酸化合物に対するアルコールのモル比は1～10倍とすることが好ましい。溶液（S）中に、Maの化合物を、溶液（S）に含まれるMd化合物のMdに対するMa化合物のMaの原子比（Ma/Md）で1未満の範囲で含有させることにより、前述のようなMaを含む酸化亜鉛系粒子を容易に得ることができる。Maを共存させることで、金属Md量（亜鉛に対する添加比）にかかわらず、単分散性に優れる微粒子が得られる効果がある。さらに、製法上、Md化合物、Zn化合物を含有する溶液（S）を得るために必要な溶媒の量を少なくすることができ、したがって、経済的に優れた条件下で目的とする酸化亜鉛系粒子が得られる。

【0031】得られる粒子の単分散性の点からMaの共存はZnに対する金属Md量が高い場合、金属Mdの種類によっても異なるが、MdがIIIB族、IVB族の場合は、Md/Zn（原子比）が3%以上、Mdが上記以外の場合は、Md/Zn（原子比）が1%以上の場合に有効である。溶液（S）の好ましい調製法として、

①予め、Md化合物を溶媒中で均一溶解し、得られた溶液（Sa）と、亜鉛化合物または亜鉛化合物を含有する液（溶液でも懸濁液でもよい）を混合し、Mdおよび亜鉛を含有する溶液（S）を得る方法

②予め、Md化合物、および亜鉛化合物の一部を溶媒中で均一溶解し、得られた溶液（Sb）と、残りの亜鉛化合物または亜鉛化合物を含有する液（溶液でも懸濁液でもよい）を混合し、Mdおよび亜鉛を含有する溶液

（S）を得る方法が挙げられる。Ma化合物は、上記の理由から、必要に応じて①の場合にはSaを調製する際に、②の場合にはSbを調製する際に添加すればよい。上記の溶液（Sa、Sb）を得るために、通常50℃以上で加熱することができ、リフラックスする温度で加熱することが好ましい。また、Sa、Sbで用いる好適な溶媒としては、前述したモノカルボン酸、このモノカルボン酸の無水物、水、前述したアルコールなどの1種または2種以上の混合物が挙げられる。

【0032】さらに、溶液（S）を、好ましくは150～200℃に加熱し、酸化亜鉛系粒子を析出させることにより、結晶子サイズの揃った、かつ凝集のない粒子の分散液が得られやすい。得られた分散液をさらに、密閉容器中で、ガス部分の雰囲気酸素濃度0.1%以下の非酸化性雰囲気下において、200℃以上400℃未満の温度で1分以上24時間以内の加熱処理を施すことにより、より結晶性が高く、膜を形成したときの赤外線遮断性および帯電防止性の付与に優れた粒子が得られる。加熱処理の温度を220～300℃の範囲とすることにより、特に単分散性に優れた粒子を得ることができる。また、酸化性雰囲気下とすると赤外線遮断性能および帯

電防止性が低下する場合があるため、好ましくない。

【0033】溶液(S)中の不純物Hの合計含有量を、亜鉛に対する原子数(ただし、硫酸根の場合はSの原子数、硝酸根の場合はNの原子数として計算する)比で0.5%以下、より好ましくは0.1%以下、さらには0.01%以下、特に0.001%以下とすることにより、前述のような不純物Hの少ない酸化亜鉛系粒子を容易に得ることができる。もちろん溶液(S)中に不純物Hを全く含まない場合も含む。

【0034】溶液(S)が、炭酸塩を、溶液(S)に含まれるZn化合物のZnに対するCO₂のモル数比で0.001~5%の範囲で含むことにより、光触媒活性の抑制された粒子を得ることもできる。以上の製法により、 $0.5 < D_s(002) / D_s(100) < 1$ 、 $0.5 \leq D_w \leq 30$ (nm)、 $0 \leq A_w \leq 0.5$ (%)を満足し、不純物Hが亜鉛に対する原子比で0.5%以下、好ましくは0.1%以下の粒子を得ることができる。〔バインダー成分〕本発明で用いられるバインダー成分は、被膜形成性能を有し、酸化亜鉛系粒子を結合して、帯電防止性に優れ、透明性、無色等の光学物性、耐久

性、密着性および可撓性に優れる塗膜を形成させる成分である。このバインダー成分は、バインダー樹脂を必須成分として含み、必要に応じて架橋剤を含むことができる。【0035】バインダー樹脂としては、熱可塑性または硬化性(熱硬化性、紫外線硬化性、電子線硬化性、湿気硬化性、これらの併用等)の各種合成樹脂や天然樹脂等を挙げることができる。合成樹脂としては、たとえば、アルキド樹脂、アミノ樹脂、ビニル樹脂、アクリル樹脂、エポキシ樹脂、ポリアミド樹脂、ポリウレタン樹脂、熱硬化性不飽和ポリエステル樹脂、フェノール樹脂、塩素化ポリオレフィン樹脂、シリコン樹脂、アクリルシリコン樹脂、フッ素樹脂、キシレン樹脂、石油樹脂、ケトン樹脂、ロジン変性マレイン酸樹脂、液状ポリブタジエン、クマロン樹脂等を挙げることができ、これらが1種または2種以上使用される。天然樹脂としては、たとえば、セラック、ロジン(松脂)、エステルガム、硬化ロジン、脱色セラック、白セラック等を挙げることができ、これらが1種または2種以上使用される。

【0036】アルキド樹脂としては、たとえば、超短油アルキド樹脂、短油アルキド樹脂、中油アルキド樹脂、長油アルキド樹脂、超長油アルキド樹脂等の純アルキド樹脂；ロジン、フェノール、エポキシ、スチレン、ウレタン、シリコン、アミノ樹脂、天然樹脂、合成樹脂、重合性モノマー等で、上記純アルキド樹脂を変性した変性アルキド樹脂；オイルフリーアルキド樹脂、高分子量オイルフリーアルキド樹脂を含むオイルフリーアルキド樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0037】アミノ樹脂としては、たとえば、ブチル化

メラミン樹脂、メチル化メラミン樹脂、ベンゾグアナミン樹脂等のメラミン樹脂・メラミンホルムアルデヒド樹脂；ブチル化尿素樹脂、ブチル化尿素メラミン樹脂等のユリア樹脂・尿素樹脂；メラミン樹脂や尿素樹脂とアルキド樹脂とを共縮合したアミノアルキド共縮合樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0038】ビニル樹脂としては、たとえば、ポリ塩化ビニル、塩化ビニルと他の重合性モノマー(酢酸ビニル、プロピオン酸ビニル等の低級脂肪酸ビニルエステル、塩化ビニリデン等)との共重合体等の塩化ビニル樹脂；ポリ酢酸ビニル、酢酸ビニルと他の重合性モノマー(エチレン、プロピレン、スチレン、アクリル酸エステル、プロピオン酸ビニル、塩化ビニリデン等)との共重合体等の酢酸ビニル樹脂；各種ケン化度のポリビニルアルコール、各種変性(シリコン変性、カルボキシル変性、アミノ変性、エポキシ変性、メルカプト変性等)ポリビニルアルコール等のポリビニルアルコール樹脂；ポリビニルブチラール、ビニルブチラールと他の重合性モノマー(ビニルアルコール、酢酸ビニル等)との共重合体等のブチラール樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0039】上記アクリル樹脂としては、たとえば、(メタ)アクリル酸およびそのエステルを主鎖の主成分とする共重合体；(メタ)アクリル酸エステルの共重合体、(メタ)アクリル酸エステルとビニル系モノマー(スチレン、ビニルエステル等)等の重合性モノマーとの共重合体等の熱可塑性アクリル樹脂；熱可塑性アクリル樹脂を構成するモノマーに、(メタ)アクリル酸、(メタ)アクリル酸のヒドロキシアシルエステル、(メタ)アクリル酸のグリシジルエステル等の架橋剤成分または加熱硬化成分を付加したもの等の熱硬化性アクリル樹脂；(メタ)アクリル系モノマー以外のスチレン、ビニルトルエン、酢酸ビニル等のモノマーで変性された共重合体、加水分解性のシリル基(アルコキシシリル基)を有するアクリルモノマーを共重合成分とする湿気硬化が可能で、樹脂中に含まれるケイ素濃度が1重量%以下であるシリル変性樹脂；塩基性窒素を有するアクリルモノマーを共重合成分とし架橋剤成分にエポキシ化合物を使用するエポキシ硬化型アクリル樹脂；酸化重合機能を有するアクリル樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0040】エポキシ樹脂としては、たとえば、ビスフェノールA型、ビスフェノールF型、2,6-キシレンール型、臭素化ビスフェノールA型、フェノールノボラック型、オルソクレゾールノボラック型等のグリシジルエーテル型；ダイマー酸等の合成脂肪酸のグリシジルエステル型；芳香族アミン型(グリシジリアミン型)等を挙げることができ、これらが1種または2種以上使用される。

【0041】バインダー樹脂としてエポキシ樹脂を用いる場合には、硬化剤を併用してもよい。硬化剤としては、たとえば、ポリメルカプタン、脂肪族ポリアミン、芳香族ポリアミン、ポリアミド、3級アミン、ジエチルアミノプロピルアミン、イミダゾール、3級アミン塩、脂環式アミン、酸無水物、フッ化ホウ素・アミン塩、ジシアンジアミド、ポリフェノール等を挙げることができ、これらが1種または2種以上使用される。

【0042】ポリウレタン樹脂としては、たとえば、油変性型、湿気硬化型、加熱硬化型、ラッカー型等の1液型ポリウレタン樹脂；ポリオール硬化型（アクリルポリオール、ポリエステルポリオール、ポリエーテルポリオール等の各種ポリオールとイソシアネートプレポリマーの組み合わせ）、触媒硬化型等の2液型ポリウレタン樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0043】フェノール樹脂としては、たとえば、レゾール型フェノール樹脂、ノボラック型フェノール樹脂や、これらフェノール樹脂をエポキシ樹脂、アルキド樹脂、ポリビニルブチラル樹脂、ポリアミド、アクリル樹脂、乾性油、ロジン、石油樹脂等で変性したもの等を挙げることができ、これらが1種または2種以上使用される。

【0044】塩素化ポリオレフィンとしては、たとえば、塩素化ポリエチレン樹脂、塩素化ポリプロピレン樹脂、塩化ゴム等を挙げることができ、これらが1種または2種以上使用される。シリコン樹脂（オルガノポリシロキサン）としては、たとえば、ジメチルシリコン、メチルフェニルシリコン等のストレートシリコン樹脂；アルキド変性、エポキシ変性、ポリエステル変性、アクリル変性、ウレタン変性された変性シリコン樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0045】アクリルシリコン樹脂は、樹脂中に含まれるケイ素濃度が1重量%以上のものであり、たとえば、ケイ素濃度が1重量%以上のアルコキシシリル基含有アクリル系共重合体等を挙げることができ、これらが1種または2種以上使用される。フッ素樹脂としては、たとえば、ポリビニルフルオライド、ポリビニリデンフルオライド、クロロトリフルオロエチレン共重合体、テトラフルオロエチレン・ヘキサフルオロプロピレン共重合体、エチレン・クロロトリフルオロエチレン共重合体、テトラフルオロエチレン・パーフルオロアルキルビニルエーテル共重合体等の熱可塑性フッ素樹脂；テトラフルオロエチレン等のフルオロオレフィンとアルキルビニルエーテル、ヒドロキシアリルビニルエーテル、カルボキシアリルビニルエーテル等のビニルエーテルとの交互共重合体（F E V E樹脂）等の溶剤可溶性フッ素樹脂；ビニリデンフルオライド・ヘキサフルオロプロピレン共重合体、テトラフルオロエチレン・プロピレン共

重合体、含フッ素シリコン系フッ素ゴム、含フッ素ビニルエーテル系フッ素ゴム、含フッ素フォスファゼン系フッ素ゴム、含フッ素サーモプラスチックエラストマー等のフッ素ゴム；含フッ素エポキシ樹脂、含フッ素ポリイミド、含フッ素シリコン等のその他フッ素ゴム等を挙げることができ、これらが1種または2種以上使用される。

【0046】熱可塑性フッ素樹脂は、溶剤に溶解しないものもあるが、水および/または有機溶剤に分散させたり、粉体の形態で用いられる。ヒドロキシル基等の架橋成分を導入した溶剤可溶性フッ素樹脂は、イソシアネートやメラミン樹脂で硬化することができる。キシレン樹脂としては、たとえば、未変性キシレン樹脂；フェノール変性、ロジン変性等の変性キシレン樹脂等を挙げることができ、これらが1種または2種以上使用される。

【0047】石油樹脂としては、たとえば、炭素数9系の石油樹脂；炭素数5系の石油樹脂等を挙げることができ、これらが1種または2種以上使用される。合成樹脂として、エチレン-プロピレン共重合ゴム、ポリブタジエンゴム、スチレン-ブタジエンゴム、アクリロニトリル-ブタジエン共重合ゴム等の天然または合成のゴム等を用いてもよい。合成樹脂と併用する成分として、硝酸セルロース、セルロースアセテートブチレート、酢酸セルロース、エチルセルロース、ヒドロキシプロピルメチルセルロース、ヒドロキシアリルセルロース等を挙げることができる。

【0048】帯電防止塗料組成物に用いられるバインダー樹脂の形態については、特に限定はなく、溶剤可溶性、水溶性型、エマルション型、分散型（水/有機溶剤等の任意の溶剤）等を挙げることができる。水溶性型のバインダー樹脂としては、たとえば、水溶性アルキド樹脂、水溶性アクリル変性アルキド樹脂、水溶性オイルフリーアルキド樹脂（水溶性ポリエステル樹脂）、水溶性アクリル樹脂、水溶性エポキシエステル樹脂、水溶性メラミン樹脂等を挙げることができる。

【0049】エマルション型のバインダー樹脂としては、たとえば、（メタ）アクリル酸アルキル共重合ディスパーション；酢酸ビニル樹脂エマルション、酢酸ビニル共重合樹脂エマルション、エチレン-酢酸ビニル共重合樹脂エマルション、アクリル酸エステル（共）重合樹脂エマルション、スチレン-アクリル酸エステル（共）重合樹脂エマルション、エポキシ樹脂エマルション、ウレタン樹脂エマルション、アクリル-シリコンエマルション、フッ素樹脂エマルション等を挙げることができる。

【0050】本発明の帯電防止塗料組成物を後述の帯電防止フィルムの製造等に用いる場合、成膜温度等の成膜条件や、得られるフィルムの可撓性や耐候性の観点からは、バインダー樹脂としては、ポリウレタン樹脂、アクリル樹脂、フッ素樹脂等が好ましい。バインダー成分と

して用いられる架橋剤としては、たとえば、空気（酸素）等の乾性油系に用いられる架橋剤；単官能または多官能の不飽和モノマー等のポリエステル樹脂、ポリアクリル樹脂、エポキシ樹脂に用いられる架橋剤；1級、2級アミノ基を含むポリアミン、ポリアミドや、メチロール基を有するアミノ樹脂、カルボキシル基を有する多塩基酸や高価価ポリエステル等のエポキシ基を有するバインダー樹脂に用いられる架橋剤；イソシアネート基を有するポリイソシアネート、ウレタン基を有するポリイソシアネート、メチロール基、1級および／または2級の10 アミノ基、アルコキシメチレン基を有するアミノ樹脂等の水酸基を有するバインダー樹脂に用いられる架橋剤；金属キレート剤等のカルボキシル基を有するバインダー樹脂に用いられる架橋剤；水分、多官能エポキシ化合物、水酸基含有化合物等のシリコン基を有するバインダー樹脂に用いられる架橋剤等を挙げることができ、これらが1種または2種以上使用される。

【0051】上記架橋剤のうちのポリイソシアネートとしては、たとえば、トリレンジイソシアネート、4, 4'-ジフェニルメタンジイソシアネート、ヘキサメチレンジイソシアネート、ナフチレン-1, 5-ジイソシアネート、イソホロンジイソシアネート、ジシクロヘキシルメタン-4, 4'-ジイソシアネート等のジイソシアネート；トリレンジイソシアネートとトリメチロールプロパンの付加体、ヘキサメチレンジイソシアネートとトリメチロールプロパンの付加体、イソホロンジイソシアネートとトリメチロールプロパンの付加体等の上記ジイソシアネートのトリメチロールプロパン付加体；イソシアヌレート変性トリレンジイソシアネート、イソシアヌレート変性ヘキサメチレンジイソシアネート、イソシアヌレート変性イソホロンジイソシアネート等の上記ジイソシアネートのイソシアヌレート変性物；ビウレット変性ヘキサメチレンジイソシアネート等の上記ジイソシアネートのビウレット変性物；上記ジイソシアネート、トリメチロールプロパン付加体、イソシアヌレート変性物、ビウレット変性物等をプレポリマー化、高分子化した変性物；上記ジイソシアネート、トリメチロールプロパン付加体、イソシアヌレート変性物、ビウレット変性物、プレポリマー化、高分子化した変性物中のイソシアネート基をアルコール類、フェノール類、オキシム類、10 活性メチレン化合物等で保護したブロック型ポリイソシアネート等を挙げることができ、これらが1種または2種以上使用される。

〔帯電防止塗料組成物および塗装品〕本発明にかかる帯電防止塗料組成物は、上記酸化亜鉛系粒子およびバインダー成分とを必須成分とする組成物である。

【0052】酸化亜鉛系粒子の、バインダー成分の全固形分および酸化亜鉛系粒子合計量に対する割合については、特に限定はないが、好ましくは50～95重量%、さらに好ましくは60～80重量%である。このとき、

バインダー成分には、架橋剤等の硬化剤をも含むものとする。酸化亜鉛系粒子の割合が前記全固形分合計量に対して、50重量%未満であると、透明性および帯電防止性が低下するおそれがある。他方、酸化亜鉛系粒子の割合が95重量%を超えると、透明性、無色等の光学物性、耐久性、耐候性、密着性および可撓性が低下するおそれがある。特に耐候性については、酸化亜鉛系粒子の割合が80重量%を超えると、急激に低下することがある。この問題を改善するためには、あらかじめ、酸化亜鉛系粒子に対して、シランカップリング剤処理や、前記M-X基含有ポリマー処理等の表面修飾しておくことが好ましいが、酸化亜鉛系粒子の製造コストが上昇し、バインダー成分を改良することが必要になる場合がある。

【0053】本発明の帯電防止塗料組成物が導電性補助剤をさらに含むものであると、帯電防止性を低下させることなく、酸化亜鉛系粒子の含有量を減らすことができ、しかも、帯電防止塗料組成物から得られる塗膜の耐候性、密着性、可撓性および耐久性等を向上させることができる。導電性補助剤を含む場合に酸化亜鉛系粒子の含有量を減らしても帯電防止性が低下しないのは、導電性補助剤が酸化亜鉛系粒子同士をつないでいく橋架けの役割をし、帯電防止効率が高まるためであると考えられる。

【0054】本発明で用いられる導電性補助剤としては、その表面の少なくとも一部が、金属、導電性金属酸化物、導電性有機物等の導電性物質からなるものが好ましい。導電性補助剤は、少なくとも表面が導電性物質からなるものであればよく、後述の芯材の少なくとも一部を導電性物質で被覆した導電性被覆補助剤でもよい。導電性補助剤に用いられる金属としては、たとえば、鉄、ニッケル、銅、スズ、アルミニウム、鉛、亜鉛、銀等の金属単体；ステンレス、銅・亜鉛合金、銅・スズ合金等の合金等を挙げることができ、これらが1種または2種以上使用される。

【0055】導電性補助剤に用いられる導電性金属酸化物としては、たとえば、酸化亜鉛、Sbドーパド酸化スズ、Alドーパド酸化亜鉛、Snドーパド酸化インジウム、スズ酸カドミウム、酸化レニウム等を挙げることができ、これらが1種または2種以上使用される。導電性補助剤に用いられる導電性有機物としては、たとえば、ポリアセチレン（ヨウ素等のドーパントをドーピングしたものを含む）；ポリピロール（過ヨウ素酸イオン等のドーパントをドーピングしたものを含む）；ポリチオフェン（過ヨウ素酸イオン等のドーパントをドーピングしたものを含む）；ポリアニリン（エメラルジン塩基等のドーパントをドーピングしたものを含む）；ポリパラフェニレン（AsF₆等のドーパントをドーピングしたものを含む）；ポリフェニレンビニレン；ポリアルキルチオフェン等のポリチオフェンや、ポリピロール等の複素環含有ポリマー；ポリパラフェニレン等の芳香環含有ポリ

マーに、エステル基や、アルキル基等を導入して得られる誘導体等の導電性ポリマー等を挙げることができ、これらが1種または2種以上使用される。

【0056】導電性被覆補助剤を構成する芯材としては、たとえば、白雲母、金雲母、鱗雲母、絹雲母、フッ素金雲母等の天然または合成雲母類や、セピオライト（粘土鉱物）、カオリナイト、タルク、ベントナイト、モンモリロナイト、スメクタイト、パイロフィライト等の天然または合成粘土鉱物や、ナイロン、ポリエステル等の有機質繊維や、チタン酸カリウム、ホウ酸アルミニウム、酸化チタン、炭化ケイ素、酸化第2鉄、ジンクフェライト、マグネシウムフェライト、ガラス、シリカ等を挙げることができ、これらが1種または2種以上使用される。

【0057】芯材の少なくとも一部を被覆するのに用いられる導電性物質としては、Sn、In、Zn、Sb、Cdを金属主成分とする導電性金属酸化物を挙げることができ、無色であるか、着色が少ない。導電性補助剤や、芯材の形状については、特に限定はないが、球状、楕円球状、立方体状、直方体状、ピラミッド状、板状、棒状等を挙げることができる。これらのうち、板状、棒状等の比較的アスペクト比が大きく、表面積の大きい異方性の形状であると、酸化亜鉛系粒子と接触する確率が高まり、酸化亜鉛系粒子同士をつないで帯電防止効率が高まるため、好ましい。

【0058】導電性補助剤として、入手しやすく、本発明の塗料組成物において分散しやすいものとしては、たとえば、鉄、ニッケル、銅、アルミニウム、鉛、亜鉛、ステンレス等の金属または合金ファイバーや、鱗片状銀、ブドウ状ニッケル等の金属系の導電性補助剤；針状Sbドーブ状酸化スズ粒子、テトラポット状酸化亜鉛粒子等の導電性金属酸化物系の導電性補助剤；Sbドーブ酸化スズ被覆チタン酸カリウムウイスカー、Sbドーブ酸化スズ被覆ホウ酸アルミニウムウイスカー、Sbドーブ酸化スズ被覆酸化チタンウイスカー、Sbドーブ酸化スズ被覆マイカ、ポリピロール被覆ポリエステル繊維等の導電性被覆補助剤等を挙げることができる。

【0059】本発明で用いられる導電性補助剤が板状粒子である場合、その厚み t については特に限定はないが、好ましくは $0.005 \sim 1 \mu\text{m}$ 、より好ましくは $0.008 \sim 0.5 \mu\text{m}$ 、さらに好ましくは $0.008 \sim 0.1 \mu\text{m}$ 、最も好ましくは $0.008 \sim 0.05 \mu\text{m}$ である。厚み t が $0.005 \mu\text{m}$ 未満であると、板状粒子の機械的強度が低下し、耐久性が低下するおそれがある。他方、厚み t が $1 \mu\text{m}$ を超えると、透明性が低下するおそれがある。板状粒子の長さ L についても特に限定はないが、好ましくは $0.02 \sim 50 \mu\text{m}$ 、さらに好ましくは $0.05 \sim 20 \mu\text{m}$ 、最も好ましくは $0.1 \sim 5 \mu\text{m}$ である。長さ L が $0.02 \mu\text{m}$ 未満であると、帯電防止性が低下するおそれがある。他方、長さ L が 50

μm を超えると、耐久性、密着性および可撓性が低下するおそれがある。板状粒子のアスペクト比（ L/t ）については、好ましくは $2 \sim 500$ 、さらに好ましくは $4 \sim 100$ 、最も好ましくは $6 \sim 50$ である。

【0060】本発明でいう板状とは、板（上からの投影形）の形が任意で、たとえば、円形、小判形、紡錘形、三角形、四角形、菱形、六角形、八角形、不定形等を含む形状であり、片状、薄片状、鱗片状、六角板状等であってもよい。本発明で用いられる導電性補助剤が棒状粒子である場合、その太さ d （棒状粒子の中心を通る最大太さ）については特に限定はないが、好ましくは $0.005 \sim 1 \mu\text{m}$ 、より好ましくは $0.008 \sim 0.5 \mu\text{m}$ 、さらに好ましくは $0.008 \sim 0.1 \mu\text{m}$ 、最も好ましくは $0.008 \sim 0.05 \mu\text{m}$ である。太さ d が $0.005 \mu\text{m}$ 未満であると、棒状粒子の機械的強度が低下し、耐久性が低下するおそれがある。他方、太さ d が $1 \mu\text{m}$ を超えると、透明性が低下するおそれがある。棒状粒子の長さ L についても特に限定はないが、好ましくは $0.02 \sim 50 \mu\text{m}$ 、さらに好ましくは $0.05 \sim 20 \mu\text{m}$ 、最も好ましくは $0.1 \sim 5 \mu\text{m}$ である。長さ L が $0.02 \mu\text{m}$ 未満であると、帯電防止性が低下するおそれがある。他方、長さ L が $50 \mu\text{m}$ を超えると、耐久性、密着性および可撓性が低下するおそれがある。棒状粒子のアスペクト比（ L/t ）については、好ましくは $2 \sim 500$ 、さらに好ましくは $4 \sim 100$ 、最も好ましくは $6 \sim 50$ である。

【0061】本発明でいう棒状とは、針状、糸状、繊維状、ウイスカー状、短冊状、星状、管状、線状、これらが複数集まった樹枝状、ブドウ状等を含む形状である。導電性補助剤が板状粒子および棒状粒子以外のその他形状粒子であってもよい。その他形状粒子としては、たとえば、球状、随円体状、紡錘体状、四面体状、六面体状、八面体状、十二面体状等の多面体状の粒子等を挙げることができる。その他形状粒子の3軸平均径〔 $(L+b+t)/3$ 〕は、好ましくは $0.005 \sim 10 \mu\text{m}$ 、さらに好ましくは $0.05 \sim 2 \mu\text{m}$ である。

【0062】本発明の帯電防止塗料組成物が、酸化亜鉛系粒子およびバインダー成分とともに導電性補助剤を含む場合、導電性補助剤の酸化亜鉛系粒子に対する割合（ $100 \times \text{導電性補助剤} / \text{酸化亜鉛系粒子}$ ）については、特に限定はないが、好ましくは $0.1 \sim 20$ 重量%、さらに好ましくは $0.3 \sim 5$ 重量%、最も好ましくは $0.5 \sim 3$ 重量%である。導電性補助剤の酸化亜鉛系粒子に対する割合が 0.1 重量%未満であると、帯電防止性が低下するおそれがある。他方、導電性補助剤の割合が 20 重量%を超えると、耐久性、密着性および可撓性が低下するおそれがある。

【0063】本発明の帯電防止塗料組成物が導電性補助剤を含む場合、導電性補助剤の、バインダー成分の固分および酸化亜鉛系粒子合計量に対する割合について

は、特に限定はないが、好ましくは0.05～9.5重量%、さらに好ましくは0.25～5重量%、最も好ましくは0.25～1.5重量%である。導電性補助剤の前記合計量に対する割合が0.05重量%未満であると、帯電防止性が低下するおそれがある。他方、導電性補助剤の前記合計量に対する割合が9.5重量%を超えると、透明性、耐久性、密着性および可撓性が低下するおそれがある。

【0064】本発明の帯電防止塗料組成物は、溶媒を含むものでもよく、バインダー成分の種類等によって適宜選択される。溶媒としては、たとえば、アルコール類、脂肪族および芳香族カルボン酸エステル類、ケトン類、エーテル類、エーテルエステル類、脂肪族および芳香族炭化水素類、ハロゲン化炭化水素類等の有機系溶剤；水；鉱物油；植物油、ワックス油、シリコーン油等を挙げることができ、これらが1種または2種以上使用される。

【0065】本発明の帯電防止塗料組成物は、酸化亜鉛系粒子、バインダー成分および導電性補助剤以外に、要求性能に従って、架橋剤等の硬化剤；硬化助剤等の硬化触媒；可塑剤；消泡剤・レベリング剤；チクソトロピック剤；艶消し剤；界面活性剤；難燃剤；顔料湿潤剤・分散剤；滑剤；紫外線吸収剤；光安定剤；酸化防止剤；その他（熱）安定剤；防腐剤；防かび剤；防藻剤；防食・防錆剤；染料；顔料等の添加剤を含有するものでもよい。

【0066】上記硬化剤としては、たとえば、空気（酸素）等の乾性油系に用いられる硬化剤；単官能または多官能の不飽和モノマー等のポリエステル樹脂、ポリアクリル樹脂、エポキシ樹脂に用いられる硬化剤；1級、2級アミノ基を含むポリアミン、ポリアミドや、メチロール基を有するアミノ樹脂、カルボキシル基を有する多塩基酸や高酸価ポリエステル等のエポキシ基を有する樹脂成分に用いられる硬化剤；イソシアネート基を有するポリイソシアネート、ウレタン基を有するポリイソシアネート、メチロール基、1級および／または2級のアミノ基、アルコキシメチレン基を有するアミノ樹脂等の水酸基を有する樹脂成分に用いられる硬化剤；金属キレート剤等のカルボキシル基を有する樹脂成分に用いられる硬化剤；水分、多官能エポキシ化合物、水酸基含有化合物等のシリコーン基を有する樹脂成分に用いられる硬化剤等を挙げることができ、これらが1種または2種以上使用される。

【0067】硬化剤のうちのポリイソシアネートとしては、たとえば、トリレンジイソシアネート、4,4'-ジフェニルメタンジイソシアネート、ヘキサメチレンジイソシアネート、ナフチレン-1,5-ジイソシアネート、イソホロンジイソシアネート、ジシクロヘキシルメタン-4,4'-ジイソシアネート等のジイソシアネート；トリレンジイソシアネートとトリメチロールプロパ

ンの付加体、ヘキサメチレンジイソシアネートとトリメチロールプロパンの付加体、イソホロンジイソシアネートとトリメチロールプロパンの付加体等の上記ジイソシアネートのトリメチロールプロパン付加体；イソシアヌレート変性トリレンジイソシアネート、イソシアヌレート変性ヘキサメチレンジイソシアネート、イソシアヌレート変性イソホロンジイソシアネート等の上記ジイソシアネートのイソシアヌレート変性物；ビウレット変性ヘキサメチレンジイソシアネート等の上記ジイソシアネートのビウレット変性物；上記ジイソシアネート、トリメチロールプロパン付加体、イソシアヌレート変性物、ビウレット変性物等をプレポリマー化、高分子化した変性物；上記ジイソシアネート、トリメチロールプロパン付加体、イソシアヌレート変性物、ビウレット変性物、プレポリマー化、高分子化した変性物中のイソシアネート基をアルコール類、フェノール類、オキシム類、活性メチレン化合物等で保護したブロック型ポリイソシアネート等を挙げる事ができ、これらが1種または2種以上使用される。

【0068】硬化触媒としては、たとえば、ナフテン酸亜鉛、ナフテン酸カルシウム、オクチル酸ジルコニウム等の金属ドライヤー、有機ドライヤー等の乾性油系に用いられる硬化触媒；レドックス系開始剤、増感剤（紫外線、電子線等が必要）等のポリエステル樹脂、ポリアクリル樹脂、エポキシ樹脂に用いられる硬化触媒；アミン類、金属化合物（熱が必要）や、有機酸（熱が必要）、無機酸（熱が必要な場合もある）等の水酸基を有するバインダー樹脂に用いられる硬化剤；金属化合物やアミン類（湿気や熱が必要）等のシリコーン基を有するバインダー樹脂に用いられる硬化触媒等を挙げる事ができ、これらが1種または2種以上使用される。

【0069】可塑剤としては、たとえば、フタル酸ジメチル、フタル酸ジエチル、フタル酸ジブチル、フタル酸ジオクチル、フタル酸ブチルベンジル、フタル酸ジイソデシル、リン酸トリクレシル、リン酸ジフェニルクレシル、リン酸トリフェニルセバシン酸ジブチル等を挙げる事ができ、これらが1種または2種以上使用される。

【0070】消泡剤・レベリング剤としては、たとえば、アクリル系消泡剤、アクリル系レベリング剤、ビニル系消泡剤、ビニル系レベリング剤、シリコーン系消泡剤、シリコーン系レベリング剤、鉱物系消泡剤、チクソトロピック剤（増粘剤、沈降防止剤、タレ防止剤）等を挙げる事ができ、これらが1種または2種以上使用される。

【0071】チクソトロピック剤の形態については、特に限定はなく、溶剤系用チクソトロピック剤、水系用チクソトロピック剤等を挙げる事ができる。溶剤系用チクソトロピック剤としては、たとえば、有機ベントナイト系、超微粉シリカ系、表面処理炭酸カルシウム系等の

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無機微粒子系溶剤系用チクソトロピック剤；アマイドワックス系、水添ひまし油ワックス系、ベンジリデンソルビトール系、金属石鹼（ステアリン酸亜鉛、ステアリン酸アルミニウム等）、酸化ポリエチレン系、重合植物油系、硫酸エステル系アニオン界面活性剤系、ポリエーテル・エステル型界面活性剤系、ポリカルボン酸アミン塩系等の有機系溶剤系用チクソトロピック剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0072】水系用チクソトロピック剤としては、たとえば、超微粉シリカ系、マグネシウムアルミニウムシリケート系等の無機微粒子系水用チクソトロピック剤；キサンタンガム、グアーガム、ポリアクリル酸ソーダ系、アクリル酸・アクリル酸エステル共重合体系、ポリビニルアルコール系、ポリエチレンオキサイド系、ウレタン変性ポリエーテル系等の有機系水用チクソトロピック剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0073】艶消し剤としては、たとえば、ホワイターカーボン等の含水 2 酸化ケイ素等を挙げることができ、これらが 1 種または 2 種以上使用される。界面活性剤としては、たとえば、ノニオン系（ポリエチレングリコール型、多価アルコール型等）、アニオン系（硫酸エステル型、スルホン酸型、カルボン酸型、リン酸エステル型等）、カチオン系（アミン塩型、第 4 級アンモニウム塩等）、両性系（アミン酸型、ベタイン型等）の界面活性剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0074】難燃剤としては、たとえば、3 酸化アンチモン、水酸化アルミニウム、塩素化パラフィン等を挙げることができ、これらが 1 種または 2 種以上使用される。顔料湿潤剤・分散剤としては、たとえば、溶剤系用顔料湿潤剤・分散剤、水系用顔料湿潤剤・分散剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0075】溶剤系用顔料湿潤剤・分散剤としては、たとえば、高分子量不飽和ポリカルボン酸、ポリエーテル・ポリエステルカルボン酸塩、高分子量ポリエステル酸ポリアミン塩、ポリカルボン酸塩、高分子量ポリエステル酸のアマイドアミン塩、長鎖ポリアミノアマイドリン酸、脂肪族ポリアマイド、長鎖ポリアミノアマイドと高分子ポリエステル酸の塩、高分子ポリエーテル系化合物等の各種高分子量化合物；リン酸エステル、リン酸エステル塩、脂肪族アルコール硫酸エステル塩類、スルホン化油、アルキルスルホン酸塩類等のアニオン性化合物；脂肪族アミンの塩類、第 4 級アンモニウム塩等のカチオン性化合物等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0076】水用顔料湿潤剤・分散剤としては、たとえば、高分子量ポリカルボン酸の塩、スチレン・マレイン酸共重合物の塩、ナフタレン・スルホン酸のホルマリン

縮合物、長鎖アルキル有機スルホン酸の塩、リグニンスルホン酸の塩、ポリリン酸、ポリケイ酸の塩、長鎖アルキルアミン塩、ポリエチレングリコール誘導体、ソルビタン脂肪酸エステル等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0077】滑剤としては、たとえば、脂肪族炭化水素系滑剤、高級脂肪族系アルコール・高級脂肪酸系滑剤、脂肪酸アマイド系滑剤、金属石鹼系滑剤、脂肪酸エステル系滑剤、複合滑剤等を挙げることができ、これらが 1 種または 2 種以上使用される。紫外線吸収剤としては、たとえば、ベンゾフェノン系、ベンゾトリアゾール系、シュウ酸アニリド系、シアノアクリレート系、トリアジン系等の紫外線吸収剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0078】上記光安定剤としては、たとえば、ビス（1, 2, 2, 6, 6-ペンタメチル-4-ピペリジル）セバケート、メチル 1, 2, 2, 6, 6-ペンタメチル-4-ピペリジルセバケート、ビス（2, 2, 6, 6-テトラメチル-1-オクチルオキシ-4-ピペリジル）デカンジオエート等のヒンダードアミン系光安定剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0079】上記酸化防止剤としては、たとえば、フェノール系（モノフェノール系、ビスフェノール系、高分子系等）、イオウ化合物系（ジラウリルチオジプロピオネート、ジミリスチルチオジプロピオネート等）、リン化合物系（トリフェニルボスフィン、ジフェニルイソデシルホスフェート等）等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0080】その他（熱）安定剤としては、たとえば、スズ系安定剤、鉛系安定剤、ステアリン酸系安定剤等を挙げることができ、これらが 1 種または 2 種以上使用される。スズ系安定剤としては、たとえば、ジ-*n*-オクチルスズビス（イソオクチルチオグリコール酸エステル）塩、ジ-*n*-オクチルスズマレイン酸塩ポリマー、ジ-*n*-オクチルスズジラウリン酸塩、ジ-*n*-オクチルスズマレイン酸エステル塩等のジ-*n*-オクチルスズ系安定剤；ジ-*n*-ブチルスズビスマレイン酸エステル塩、ジ-*n*-ブチルスズマレイン酸エステル塩等のマレート系化合物、ジ-*n*-ブチルスズビスオクチルチオグリコール酸エステル塩、ジ-*n*-ブチルスズβ-メルカプトプロピオン酸塩ポリマー等のメルカプト系化合物、ジ-*n*-ブチルスズジラウレート等のラウレート系化合物等のジ-*n*-ブチルスズ系安定剤；ジメチルスズビス（イソオクチルメルカプトアセテート）塩等のジメチルスズ系安定剤等を挙げることができ、これらが 1 種または 2 種以上使用される。

【0081】鉛系安定剤としては、たとえば、3 塩基性硫酸鉛、2 塩基性ステアリン酸鉛、2 塩基性亜リン酸鉛、ステアリン酸鉛等を挙げることができ、これらが 1

種または2種以上使用される。ステアリン酸系安定剤としては、たとえば、ステアリン酸バリウム、ステアリン酸カルシウム、ステアリン酸マグネシウム、ステアリン酸アルミニウム、ステアリン酸リチウム、12-ヒドロキシステアリン酸リチウム等を挙げることができ、これらが1種または2種以上使用される。

【0082】その他(熱)安定剤として、上記スズ系安定剤、鉛系安定剤、ステアリン酸系安定剤以外の安定剤を用いてもよく、このような安定剤として、たとえば、ベヘン酸リチウム、ミリスチン酸リチウム、トリフェニルホスファイト、ジフェニル・イソデシルホスファイト、トリスノニルフェニルホスファイト、バリウム-亜鉛液状複合安定剤、カルシウム-亜鉛液状複合安定剤、カドミウム-バリウム-亜鉛液状複合安定剤等を挙げることができ、これらが1種または2種以上使用される。

【0083】防腐剤、防かび剤および防藻剤としては、たとえば、1, 2-ベンズイソチアゾリン-3-オン、5-クロロ-2-メチル-4-イソチアゾリン-3-オン、p-クロロ-m-キシレノール、2-ヒドロキシメチルアミノエタノール等を挙げることができ、これらが1種または2種以上使用される。防食・防錆剤としては、たとえば、エチルアミン類、プロピルアミン類等を挙げることができ、これらが1種または2種以上使用される。

【0084】本発明の帯電防止塗料組成物は、光安定剤をさらに含むものであると、耐候性が向上する。帯電防止塗料組成物の硬化方法については、経済的に加熱硬化法が好ましい。本発明の帯電防止塗料組成物の製造方法については、特に限定はないが、たとえば、酸化亜鉛系粒子を含む分散体に、バインダー成分を混合し、適宜、導電性補助剤をさらに混合する方法等を挙げることができる。

【0085】本発明にかかる塗装品は、上記帯電防止塗料組成物から得られる塗膜を基材表面に形成してなるものである。この塗装品は、その表面に帯電防止塗料組成物から得られる塗膜を備えているために、優れた帯電防止性を有し、塗膜の耐候性、密着性および可撓性は高い。基材としては、たとえば、ガラス、陶器等の無機物や、樹脂等の有機物等の基材を挙げることができ、特に、有機物の基材表面に帯電防止塗料組成物を塗布して得られる塗膜は、耐候性が高く、可撓性に優れる。上記無機物や有機物の形状については、特に限定はなく、フィルム状、シート状、板状、繊維状等の形状を挙げることができる。これらのうちでも、後述のフィルムや、繊維等に有用である。

【0086】基材として用いられる樹脂の材質としては、特に限定はなく、たとえば、LDPE、HDPE、アモルファスポリエチレン、OPP(延伸ポリプロピレン)、CPP(結晶化ポリプロピレン)等のポリプロピレン、ポリイソブチレンなどのポリオレフィン系；E

A(エチレン・酢酸ビニル共重合体)系；ポリスチレン系；軟質又は硬質ポリ塩化ビニル；EVOH(エチレン・ビニルアルコール共重合体)系；PVA系(ビニロン系)；PVDC系(ポリ塩化ビニリデン)；ポリエチレンテレフタレート、ポリエチレンナフタレート、ポリブチレンナフタレート等のポリエステル系；ポリカーボネート系；ポリウレタン系；ポリアミド系；ポリイミド系；ポリアクリロニトリル系；ポリサルフォン系；ポリエーテルサルフォン系；ポリフェニレンサルファイド系；ポリアリレート系；ポリエーテルイミド系；アラミド系；(メタ)アクリル系；ポリエーテルエーテルケトン系；テトラフルオロエチレン・エチレン共重合体、テトラフルオロエチレン・ヘキサフルオロプロピレン共重合体、ポリテトラフルオロエチレン、ポリトリフルオロエチレン、ポリフッ化ビニリデン、ポリフッ化ビニル、テトラフルオロエチレン・ペルフルオロアルキルビニルエーテル共重合体、ポリフッ化ビニル、テトラフルオロエチレン・ヘキサフルオロプロピレン・ペルフルオロアルキルビニルエーテル共重合体、ポリクロロトリフルオロエチレンなどのフッ素系樹脂等を挙げることができる。

【0087】光学レンズ等の極めて高度な可視光透過性、透明性が要求される用途で用いる場合には、PMMMA、MMA-スチレンランダム共重合体、ポリカーボネート、透明ポリプロピレン、MMAと α -メチルスチレンまたはシクロヘキシルメタクリレート等の共重合体、ABS樹脂のMMA変性タイプ、ポリスチレン、ポリアリレート、ポリサルフォン、ポリエーテルサルフォン、透明エポキシ樹脂、ポリ-4-メチルペンテン-1、フッ素化ポリイミド、非晶質フッ素樹脂、透明フェノキシ樹脂、非晶質ナイロン樹脂、フルオレン系等の各種樹脂を基材として使用することができる。

【0088】また、廃棄処理問題から、生分解性に対する要求に応えるものとして、生分解性樹脂を基材として用いることは今後ますます重要になる。このような場合、たとえば、ポリ-3-ヒドロキシ酪酸エステル、キチン・キトサン系、ポリアミノ酸系、セルロース系、ポリカプロラクトン系、アルギン酸系、ポリビニルアルコール系、脂肪族ポリエステル系、糖類系、ポリウレタン系、ポリエーテル系などの生分解性プラスチック等を基材として用いることが好ましい。

【0089】基材としては、上記基材に予めUV吸収膜を配したもののや、帯電防止塗料組成物から得られる塗膜と基材との密着性などを高める目的で、プライマー層等を予め配したもののものでもよい。基材として用いられるこれらの樹脂のうちでも、プラスチックフィルム、シートのうち、耐候性が高い点でフッ素系樹脂、ポリエステル系樹脂、(メタ)アクリル系樹脂、ポリカーボネート系樹脂が好ましい。

【0090】本発明の塗装品は、たとえば、上記基材表

面に帯電防止塗料組成物を塗布し、硬化させることによって製造することができる。帯電防止塗料組成物を基材表面に塗布する方法については、特に限定はなく、ディッピング法、ロールコーター法、フローコート法、スクリーン印刷法、バーコーター法、スピンコーター法、刷毛塗り法、スプレー法等を挙げることができる。

【0091】帯電防止塗料組成物を塗布した後、耐水性、耐溶剤性、耐酸、耐アルカリ等の耐薬品性、耐擦傷性等の物性を向上させるために、熱硬化（室温硬化を含む）、湿気硬化、紫外線硬化、電子線硬化等の方法で硬化させることが好ましい。帯電防止塗料組成物から得られる塗膜の乾燥膜厚については、特に限定はなく、好ましくは0.5～50μm、さらに好ましくは0.2～5μm、最も好ましくは0.5～2μmである。

【0092】帯電防止塗料組成物から得られる塗膜の表面抵抗 ρ については、特に限定はないが、好ましくは $10^{10}\Omega/\square$ 以下、さらに好ましくは $10^9\Omega/\square$ 以下、最も好ましくは $10^6\sim 10^9\Omega/\square$ である。帯電防止塗料組成物から得られる塗膜のヘイズについては、特に限定はないが、好ましくは5%以下、さらに好ましくは2%以下、最も好ましくは1%以下である。ヘイズは、濁度計で測定して得られた値である。

【0093】

【実施例】以下に、本発明の実施例を比較例と合わせて示すが、なお、本発明は下記実施例に限定されるものではない。以下の実施例において、「部」と「重量部」を示す。本実施例における評価等は次の手法により行った。

1. 酸化亜鉛系粒子の評価

＜粒子組成＞粉末試料の添加金属含有量、他の金属含有量、不純物H含有量は、蛍光X線分析、原子吸光分析、プラズマ発光分析、重量分析および元素分析などにより求めた。

＜結晶性＞粉末X線回折により評価した。結晶性の評価基準は以下のとおり。

【0094】

○：ZnO結晶の回折ピークがある。

×：ZnO結晶の回折ピークがない。

＜結晶子径 $D_s(hkl)$ 、 D_w 、格子歪 A_w ＞粉末試料の粉末X線回折測定を行い求めた。

$D_s(hkl)$ ：Scherrer法（Cauchy関数近似による）によって、得られる各回折面（ hkl ）に対して垂直な方向の結晶子径

D_w 、 A_w ：Wilson法を用いて求めた結晶子の大きさ及び格子歪

＜カルボン酸基含有量＞粉末試料1gを0.01Nの水酸化ナトリウム水溶液に混合し、3日間攪拌した後、遠心分離操作によって得た上澄みをイオンクロマト分析することによって測定した。

＜分散体の粒子濃度＞分散体の一部を100℃において

溶媒等の揮発成分を完全に除去し得るまで真空乾燥することにより乾燥粉末を得、これを空气中、500℃で1時間加熱したときの残分を金属酸化物として、金属酸化物分の分散体に対する重量分率を求め、この値を分散体中の粒子濃度（金属酸化物換算濃度）とした。

2. 帯電防止塗料組成物から得られる塗膜の評価

＜表面抵抗＞塗膜表面に、金の櫛形電極を蒸着（厚み30nm±5nm）し、表に示す温湿度条件下、遮光条件下で12時間放置した後、ケスレー社製エレクトロメーター617型を用いて、同条件下における表面抵抗値を測定（印加電圧0.1V）した。表面抵抗の測定は、表に示した測定条件（1）および（2）で行った。

【0095】促進耐候性試験後の塗膜の表面抵抗は、JIS B 7753-93に記載のサンシャインカーボンアーク灯式耐光性および耐候性試験機を用いて、促進耐候性試験を200時間行い、その後の表面抵抗を測定した。耐水試験後の表面抵抗は、純水の沸騰水に10時間浸漬し、その後の表面抵抗を測定した。

＜可視光透明性および透明性＞濁度計（日本電色工業（株）製NDH-1001 DP）により、全光線透過率TおよびヘイズHを測定した。

＜透明耐久性＞促進耐候性試験後の透明性は、JIS B 7753-93に記載のサンシャインカーボンアーク灯式耐光性および耐候性試験機を用いて、促進耐候性試験を200時間行い、その後に測定した。透明性の測定には、濁度計（日本電色工業（株）製、NDH-1001 DP）を用い、初期ヘイズ値 H_0 と試験後のヘイズ値 H との差 $\Delta H(\%) = H - H_0$ を求め、下記の評価基準で判定した。透明性の評価基準は以下のとおり。

【0096】

AA： $\Delta H < 1\%$

A： $1\% \leq \Delta H < 5\%$

B： $5\% \leq \Delta H < 10\%$

C： $10\% \leq \Delta H$

3. 帯電防止塗料組成物の評価

＜分散性＞帯電防止塗料組成物等における酸化亜鉛系粒子の分散性は動的光散乱方式による粒子系アナライザー（野崎産業（株）NICOMP Model 370）を用いて、重量基準の平均粒子径を求め、これを平均分散粒径 D_d とした。分散性の評価基準は以下のとおり。但し、架橋剤や硬化触媒を添加する系では、これらを添加する前に、分散性を測定した。

【0097】

A： $D_d \leq 30\text{nm}$

B： $30\text{nm} < D_d \leq 50\text{nm}$

C： $50\text{nm} < D_d \leq 100\text{nm}$

D： $100\text{nm} < D_d$

＜分散安定性＞帯電防止塗料組成物をバス温度50℃に浴槽に浸漬した状態で、30日間静置した後の分散体の外観を評価した。分散安定性の評価基準は以下のとお

り。

【0098】

A：層分離せず、沈降物のない状態。

B：沈降物はあるが、振盪により再分散する。

C：沈降し、振盪しても再分散せず、ゲル化する。

＜ポットライフ＞帯電防止塗料組成物を製造する際、架橋剤を添加した後、20℃で攪拌し、1時間ごとに成膜した。得られた塗膜について、それぞれ、透明性および硬化性を調べ、これらの物性が悪化しない攪拌時間の上限Tを測定した。ポットライフの評価基準は以下のとおり。

【0099】

A：T＞6時間

B：6時間≧T＞3時間

C：T≦3時間

＜硬化性＞メチルエチルケトンを含浸させた綿を塗膜上に100回擦り、ラビングテストを行った。テスト後の塗膜の表面状態を観察した。硬化性の評価基準は以下のとおり。

【0100】

○：変化なし。

△：表面に傷がみられる。

×：塗膜が溶解する。

*

分散体D1（粒子濃度50重量％）

40重量部

バインダーB1（不揮発分濃度35％）

14.3重量部

レベリング剤（ポリシロキサン系）

0.05重量部

トルエン

35重量部

上記で得られた帯電防止塗料組成物C1をPETフィルムの表面にバーコーターで塗布し、80℃で2分間、熱風乾燥した後、50℃で3日間養生して、乾燥膜厚0.5μmの塗膜（1）を得た。塗膜（1）の各種物性を評価し、その結果を表7に示す。

【0104】－実施例1（2）～1（7）－

表1に示す物性の酸化亜鉛系粒子P2～P5を表2に示す表面修飾を行って、表2に示す溶媒に分散させて、分

*＜密着性＞塗膜について、セロハンテープによる碁盤目剥離試験を行い、密着性を調べた。密着性の評価基準は以下のとおり。

【0101】

A：100/100（全く剥離なし）

B：80/100以上100/100未満

C：50/100以上80/100未満

D：50/100未満

＜可撓性＞3回90度折り曲げを行い、表面に発生するクラックや、剥離の有無をマイクロスコープで観察した。可撓性の評価基準は以下のとおり。

【0102】○：変化なし。

△：剥離はしないが、クラックが発生する。

×：剥離する。

－実施例1（1）－

表1に示す物性の酸化亜鉛系粒子P1を表面修飾することなく、トルエンに分散させて、分散体D1（粒子濃度50重量％）を調製した。この分散体D1に、表3に示すバインダーB1等を下記に示す配合で混合し、25℃で3時間攪拌して帯電防止塗料組成物C1を得た。帯電防止塗料組成物C1の物性を表5に示す。

【0103】

分散体D2～D5を調製した。これらの分散体D2～D5に、それぞれ、表3に示すバインダーB2～B7等を表4に示す配合で混合添加し、実施例1（1）と同様にし、帯電防止塗料組成物C2～C7を得た。帯電防止塗料組成物C2～C7の物性を表5に示す。

【0105】

【表1】

酸化亜鉛系粒子	添加金属含有量 (Zn基準)		粉末X線解析結果			結晶性	不純物H含有量 (Zn基準) モル%	他金属含有量 (Zn基準)		カルボン酸基含有量 重量%
	Md	モル%	Dw nm	Ds比 002/100	Aw %			金属	モル%	
P1	Al	1	20	0.79	0.10	○	<0.001	0		3.1
P2	In	4	12	0.60	0.01	○	<0.001	Na	0.1	0.5
P3	Ga	2.5	15	0.89	0.10	○	<0.001	Li	0.3	0.9
P4	Y	0.5	30	0.90	0.22	○	<0.001	Mg	0.2	4.3
P5	Hf	0.9	18	0.93	0.22	○	<0.001	0		2.4
P6	Ga	2.0	22	1.29	0.28	○	Cl:1.09	0		<0.001

【0106】

* * 【表2】

酸化亜鉛系粒子	表面修飾剤	処理量	分散体	分散体組成	
		(酸化亜鉛系粒子基準) 重量%		粒子濃度 酸化物換算*1 重量%	溶媒
P 1	なし	—	D 1	5 0	トルエン
P 2	重合体 A * ²	1 0 . 0	D 2	4 0	トルエン
P 3	カルキル変性ポリメチルシロキサン	1 . 0	D 3	4 0	酢酸ブチル
P 4	アルキルセートアルミニウムイソプロピレート	2 . 4	D 4	2 0	酢酸ブチル
P 5	ヒドロキシチルトリエチシラン	1 8	D 5	3 0	イソブチル
P 6	なし	—	D 6	1 0	トルエン

*1: 600℃焼成時の灰分重量から求めた。

*2: 重合体Aは、メチルメタクリレート(20部)、シロキシメタクリレート(75部)およびメタクロキシプロピルトリエチシラン(5部)を重合して得られた重合体

【0107】

【表3】

バインダー種類		備 考		
		酸価	数平均 分子量	OHV
B 1	アクリル樹脂	0.5	30,000	- HALSハイブリッドタイプ
B 2	アクリル樹脂	2	6,000	40 HALSハイブリッドタイプ
B 3	フッ素樹脂	2.5	10,000	24
B 4	ポリウレタン樹脂 (ポリエステルポリオール)	8	3,000	250
B 5	水溶性アクリル樹脂	pH 8	-	- アミン中和タイプ
B 6	アクリルシリコン樹脂	-	12,000	- Si-OCH ₃ 基含有
B 7	紫外線硬化型 ウレタンアクリレート	0.1	-	-

【0108】

【表4】

実施例1	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	主溶媒	他の添加剤
(1)	C1	D1	B1	なし	28	78	トルエン	レベリング剤
(2)	C2	D2	B2	架橋剤A*3	45	73	トルエン	レベリング剤
(3)	C3	D2	B3	架橋剤A*3	35	80	トルエン	レベリング剤
(4)	C4	D4	B4	架橋剤A*3	50	80	酢酸ブチル	—
(5)	C5	D5	B5	なし	50	77	イソプロパノール	—
(6)	C6	D5	B6	なし	30	70	イソプロパノール	ジブチルスズラケート
(7)	C7	D3	B7	なし	60	82	酢酸ブチル	—

*1: 600℃焼成時の灰分重量から求めた酸化物換算濃度。

*2: 固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

*3: 架橋剤Aは、イソシアレート変性ヘキサメチレンジイソシアネートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアネート基がモル比で、1:1となるように添加した。

【0109】

【表5】

	帯電防止塗料組成物	塗膜	帯電防止塗料組成物物性			塗膜物性		
			分散性	分散安定性	ポットライフ	硬化性	密着性	可撓性
実施例1(1)	C1	(1)	A	A	A	×	B	○
実施例1(2)	C2	(2)	A	A	A	○	A	○
実施例1(3)	C3	(3)	A	A	B	○	A	○
実施例1(4)	C4	(4)	B	B	B	○	A	—
実施例1(5)	C5	(5)	B	B	A	△	B	—
実施例1(6)	C6	(6)	A	B	B	○	B	—
実施例1(7)	C7	(7)	A	B	A	○	A	○
比較例1	C11	(11)	D	B	A	○	D	△

【0110】帯電防止塗料組成物C2～C7を、それぞれ、表6に示す条件で成膜し、塗膜(2)～塗膜(7)を得た。なお、表6には、帯電防止塗料組成物C1から塗膜(1)を得る成膜条件も示した。得られた塗膜(2)～塗膜(7)の物性を評価し、その結果を表7に示す。

【0111】

【表6】

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実施例1	塗膜	帯電防止塗料組成物	基 材	乾燥条件	膜 厚 ドライ μm
(1)	(1)	C1	PETフィルム	80℃、2分間	0.5
(2)	(2)	C2	PETフィルム	100℃、2分間	1
(3)	(3)	C3	フッ素フィルム	100℃、2分間	3
(4)	(4)	C4	PMMA板	60℃、1時間	6
(5)	(5)	C5	ガラス	80℃、5分間	3
(6)	(6)	C6	PC板	常温、1カ月	5
(7)	(7)	C7	PETフィルム	*1	1

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*1：高圧水銀灯(80W/cm)、距離15cmで、5秒間

【0112】

【表7】

実施例1	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性		透明耐 久性 促進耐 候性試 験後
		環境条件 (1)	環境条件 (2)	環境条件 (1)				
				促進耐 候性試 験後	耐水試 験後			
(1)	(1)	4.4X10 ⁷	3.9X10 ⁷	8.0X10 ⁷	7.1X10 ⁷	86	3.3	A
(2)	(2)	8.7X10 ⁷	8.0X10 ⁷	9.0X10 ⁷	8.8X10 ⁷	87	2.5	AA
(3)	(3)	1.9X10 ⁸	2.0X10 ⁸	1.9X10 ⁸	1.8X10 ⁸	92	3.0	AA
(4)	(4)	3.2X10 ⁸	3.2X10 ⁸	5.5X10 ⁸	3.3X10 ⁸	89	1.0	A
(5)	(5)	7.1X10 ⁸	6.8X10 ⁸	>10 ⁹	>10 ⁹	88	0.8	C剝離
(6)	(6)	1.6X10 ⁸	9.9X10 ⁷	4.0X10 ⁸	3.2X10 ⁸	87	2.4	B
(7)	(7)	3.5X10 ⁸	3.1X10 ⁸	3.6X10 ⁸	3.6X10 ⁸	87	2.7	A

環境条件 (1) : 10℃、相対湿度20%

環境条件 (2) : 30℃、相対湿度60%

【0113】—実施例2(1)—

実施例1(1)で用いた分散体D1(粒子濃度50重量%)およびバインダーB1等に、導電性補助剤としてのウィスカー状粒子粉末(チタニアウィスカー表面にアンチモン含有酸化スズ被膜を形成したもの、長さ:2 μ m、直径:0.1 μ m、アスペクト比:20)を添加し、表8に示す組成の帯電防止塗料組成物C8を調製した。帯電防止塗料組成物C8を表9に示す成膜条件で、
塗膜(8)を得た。得られた塗膜(8)の物性を評価し、その結果を表10に示す。

【0114】—実施例2(2)—

実施例1(2)で用いた分散体D2およびバインダーB2等に、導電性補助剤としてのウィスカー状粒子粉末(ホウ酸アルミニウムウィスカー表面にアンチモン含有酸化スズ被膜を形成したもの、長さ:18 μ m、直径:0.8 μ m、アスペクト比:20)を添加し、表8に示す組成の帯電防止塗料組成物C9を調製した。帯電防止塗料組成物C9を表9に示す成膜条件で、
塗膜(9)を得た。得られた塗膜(9)の物性を評価し、その結果を表10に示す。

【0115】—実施例2(3)—

実施例1(2)で用いた分散体D2およびバインダーB3等に、導電性補助剤としてのウィスカー状粒子粉末(アンチモンドープ酸化スズウィスカー、長さ:2.0 μ m、直径:0.01 μ m、アスペクト比:200)を添加し、表8に示す組成の帯電防止塗料組成物C10を調製した。帯電防止塗料組成物C10を表9に示す成膜条件で、
塗膜(10)を得た。得られた塗膜(10)の物性を評価し、その結果を表10に示す。

【0116】—比較例1—

実施例1(1)で用いた酸化亜鉛系粒子P1の代わりに、表1に示した物性の粒子P6を用いる以外は、実施例1(1)と同様にして、帯電防止塗料組成物C11を調製した。帯電防止塗料組成物C11の物性を表5に示す。帯電防止塗料組成物C11を、実施例1(1)と同様に、PETフィルムに成膜して、
塗膜(11)を得た。得られた塗膜(11)の物性を評価し、その結果を表10に示す。

【0117】

【表8】

実施例2	帯電防止塗料組成物	分散体	バインダー	架橋剤	固形分濃度 *1 重量%	粒子濃度 *2 重量%	導電性補助剤*3/酸化亜鉛系粒子 重量%	主溶媒	他の添加剤
(1)	C8	D1	B1	なし	28	75	1	トルエン	レベリング剤
(2)	C9	D2	B2	架橋剤A*4	25	65	2	トルエン	レベリング剤
(3)	C10	D2	B3	架橋剤A*4	55	70	4	トルエン	レベリング剤

*1: 600℃焼成時の灰分重量から求めた酸化物換算濃度。

*2: 固形分に対する濃度。固形分は、酸化亜鉛系粒子、バインダーおよび架橋剤の和である。

*3: 導電性補助剤として、実施例2(1)～2(3)に記載したウィスカー状粒子粉末を用いた。

*4: 架橋剤Aは、イソシアレート変性材料イソシアネートであり、その添加量はバインダー中の水酸基と架橋剤Aのイソシアネート基がモル比で、1:1となるように添加した。

【0118】

【表9】

実施例2	塗膜	帯電防止塗料組成物	基材	乾燥条件	膜厚 ドライ μm
(1)	(8)	C8	PET74μm	80℃、2分間	0.5
(2)	(9)	C9	PET74μm	100℃、2分間	1
(3)	(10)	C10	フッ素74μm	100℃、2分間	3

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【表10】

	塗 膜	表面抵抗 (Ω/□)				可視光透過性 および透明性		透明耐 久性
		環境条件 (1)	環境条件 (2)	環境条件 (1)				
				促進耐候 性試験後	耐水試験 後	T (%)	H (%)	促進耐 候性試 験後
実施例 2 (1)	(8)	8.8X10 ⁶	8.4X10 ⁶	9.0X10 ⁶	8.8X10 ⁶	85	3.8	A
実施例 2 (2)	(9)	2.2X10 ⁷	2.0X10 ⁷	3.0X10 ⁷	2.8X10 ⁶	84	4.2	AA
実施例 2 (3)	(10)	3.0X10 ⁶	2.8X10 ⁶	3.7X10 ⁶	3.9X10 ⁶	88	3.6	AA
比較例 1	(11)	1.2X10 ⁷	1.3X10 ⁷	—	—	82	22	C

環境条件 (1) : 1 0℃、相対湿度 2 0%

環境条件 (2) : 3 0℃、相対湿度 6 0%

【0 1 2 0】

【発明の効果】本発明にかかる帯電防止塗料組成物は、湿度、温度等に対する依存性が低く、長期間安定した帯電防止性を有し、透明性、無色等の光学物性、耐久性、

密着性および可撓性に優れる塗膜を形成できる。本発明にかかる塗装品は、長期間安定した帯電防止性を有し、その表面に形成された塗膜は、透明性、無色等の光学物性、耐久性、密着性および可撓性が高い。